A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

STABILITY AND MECHANISM OF DEGRADATION OF SOME BROMINATED COPOLYMERS

BY

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SUMMARY

The non-flammability properties of halogenated polymeric materials has been given a great deal of attention in the last few years, their thermal decomposition and thermal stability properties having been of particular interest.

This present work involves the thermal degradation of 2,3 - dibromopropyl methacrylate (2,3 - D B P M) and 2,3 - dibromopropyl acrylate (2,3 - D B P A) in different copolymer and polymer blend environments.

A brief description of the various ways in which a fire retardant may effect a burning polymer is presented in Chapter 1. The preparation of polymeric materials is described in Chapter 2 together with a description of the apparatus and experimental techniques which were employed.

Two methods for obtaining compositions of the copolymers are described and evaluated in Chapter 3 and reactivity ratios for the comonomers are reported.

Chapter 4 reports that the thermal degradation of P2,3 - D B P M is principally a depolymerisation process giving monomer, although some ester decomposition also occurs. On the other hand the thermal degradation of P2,3 - D B P A yields hydrogen bromide, carbon dioxide, allyl bromide, chain fragments, alcohols and some other minor products.

Chapter 5 presents the results of a study of the thermal degradation of copolymers of 2,3 - D B P M and 2,3 - D B P A with methyl methacrylate (M M A). The presence of compounds such as methyl bromide and methanol among the products provides evidence for interaction

between the two monomer units in the degrading copolymer molecules. A qualitative and quantitative study of the thermal degradation of copolymers of 2,3 - D B P M and 2,3 - D B P A with styrene (S) is described in Chapter 6, and suggests that no interaction takes place between either of these monomer units during the copolymer decomposition.

Chapter 7 describes the thermal degradation of copolymers of 2,3 - D B P M and 2,3 - D B P A with methyl acrylate (M A). In this case interaction between the monomer units results methyl bromide and anhydride structures. Similar structures also occur in blends of P2,3 - D B P M and P2,3 - D B P A with P M M A and P M A (Chapter 8). Mechanisms of all the decompositions and interactions are proposed and discussed.

All the results are summarised in Chapter 9 , and suggestions made for future work.

C O N T E N T S

CHAPTER 1

INTRODUCTION

In recent years, the flammability properties of materials, especially synthetic organic polymers, have become a major topic of research in the commercial and academic fields with the aim of producing materials which retard the burning process. The chemistry of fire retardants centers around six elements, namely, phosphorous, antimony, chlorine, bromine, boron and nitrogen.

Fire retardant polymeric materials can be divided into two general classes :

a. Those in which the fire retarding agent is in the form of an additive which is mixed with the polymer. An example of this is the incorporation of ammonium polyphosphate into polyurethane foams.[1]

b. Those in which the fire retardant is incorporated into the macromolecular chain structure of the polymer during the polymerisation process. For example, acrylic fibres which are basically polyacrylonitrile may incorporate some vinylidene chloride or vinyl bromide[2] as comonomers.

There are various general mechanisms of fire retardance in polymeric materials [3,4].

i. A heat barrier may be formed by physically covering the polymer with a reflecting intumescent coating which reduces heat transfer from the heat source to the polymer so that polymer degradation is inhibited.

ii. The concentration of combustible gases may be diluted by the production of inert species such as carbon dioxide and nitrogen.

iii. A dust may be produced which acts as a heterogeneous catalyst

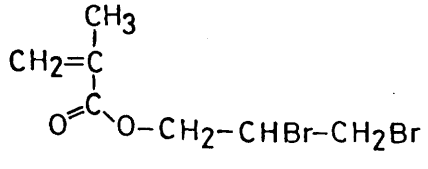
in deactivating the radicals involved in flame propagation.

iv. The proportion of volatile inflammable products may be reduced and the proportion of involatile char increased.

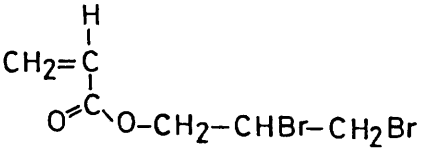
v. The degradation and decomposition reactions may be modified to produce non-flammable volatiles (usually halogenated species). The last of these is perhaps the most important of the flame retardant mechanisms because of the relatively small proportion of chemical flame retardant required for a significant effect. Unlike inert gases, halogens or halogen derivatives strongly affect the flame velocity in concentrations of less than one per cent. The flame propagating cycle involves radical species such as $H^{\bullet}$ and $OH^{\bullet}$ radicals. Halogen compounds react with these radicals in the following way :

$$RX + H^{\bullet} \longrightarrow HX + R.$$

The radical R• will be less reactive than the $H^{\bullet}$ radical which it replaces so this substitution results in flame inhibition. The effectiveness of halogen compounds as flame-retardants is in order I , Br> Cl≫ F. Bromine acting primarily in the flame zone, while chlorine functions partially in slowing condensed phase reactions. Bromine is found to be twice as effective as chlorine on a weight basis or about four times on a mole basis. The evolution of halogenated pyrolysis products also removes heat from the flame reaction zone which in turn assists in the inhibition of further combustion. The work described in this thesis is concerned with the products and mechanisms of degradation of the homopolymersand some copolymersand blends of the two bromine containing monomers, 2,3 - dibromopropyl methacrylate (2,3 - D B P M) and 2,3 - dibromopropyl acrylate (2,3 - D B P A).



2,3-DBPM



2,3-DBPA

It is anticipated that studies of this kind may provide a better understanding of the chemistry and reaction mechanism involved in existing commercial fire-retardant systems and contribute to a fund of information which may assist in the formulation of new fire-retarding polymer systems. Such studies should make it possible to determine the optimum conditions for maximum effectiveness of the fire-retardant with minimum loss of the physical properties of the parent polymer. The degradation reactions were carried out either under high vacuum conditions or in a dynamic inert atmosphere, to assist in the removal of primary decomposition products, and to study the primary chemical processes which take place during the thermal decomposition stage.

A qualitative and quantitative study of the degradation products was carried out in order to determine the nature and extent of any interactions which may occur between the comonomer units or between the mixed polymers. These studies will ultimately lead not only to an understanding of the mechanism of degradation of the various copolymers and blends but also provide useful information on the respective homopolymer decomposition mechanism. It is anticipated that information of this kind will be relevant to the use of bromine containing compounds in fire-retardant polymer compositions.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2. 1 INTRODUCTION

This chapter will include information on the purification of monomers, the preparation of polymers and the thermal analysis techniques and analytical equipment used in the qualitative and quantitative determination of the degradation products.

2. 2 MATERIALS

i. Purification of Monomers

a. 2,3 - Dibromopropyl methacrylate (2,3 - D B P M) and 2,3 - dibromopropyl acrylate (2,3 - D B P A) (Polysciences Ltd) were purified by distillation under vacuum as shown in figure 2.1, using hydroquinone as inhibitor.

b. Methyl methacrylates (M M A) (Hopkin and Williams Ltd), styrene (S) (B P Chemicals International Ltd) and methyl acrylate (M A) (BDH Chemicals Ltd), were washed with caustic soda solution to remove the inhibitor, subsequently with distilled water and dried over calcium hydride. The monomers were vacuum distilled twice, the first and last 20% being eliminated.

All the monomers were stored in the dark at $-18^{o}C$ until used.

ii. Purification of Initiator

2,2´-Azobisisobutyronitrile (AIBN) (Eastoman Kodak) was used as initiator (0.1 per cent $\frac{w}{v}$) for all polymerisations. It was purified by dissolving in hot ethonol[5] and filtering. The solution was left to cool, the crystals of the pure material being collected by filtration and dried under vacuum.

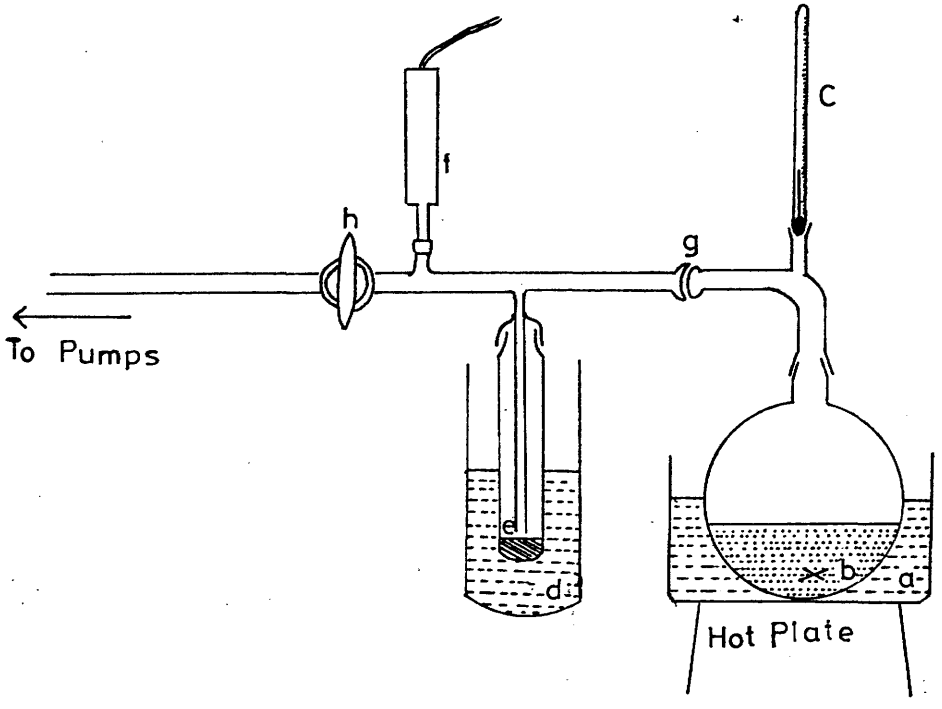


Fig.2.1. Purification Apparatus.

(a) Water bath
(b) Unpurified monomer with stirrer
(c) Thermometer
(d) Liquid nitrogen Dewer flask
(e) Purified monomer
(f) Pirani gauge
(g) Flange
(h) Stopcock

iii. Purification of the Solvent

Methyl acetate (B D H Ltd) was used as solvent in the polymerisations. It was purified by drying over calcium hydride for four days and twice distilled under vacuum, the first and last 20% being eliminated.

2. 3 PREPARATION and PURIFICATION of the POLYMERS

i. Preparation of Homopolymers and Copolymers

The following homopolymers and copolymers were prepared

HOMOPOLYMERS	COPOLYMERS
a. 2,3 - D B P M	e. 2,3 - D B P M - M M A
b. 2,3 - D B P A	f. 2,3 - D B P A - M M A
c. M M A	g. 2,3 - D B P M - S
d. M A	h. 2,3 - D B P A - S
	i. 2,3 - D B P M - M A
	j. 2,3 - D B P A - M A

These homopolymers and copolymers were prepared by free radical initiation using methyl acetate ($\frac{50}{50}$ % $\frac{V}{V}$) as solvent. Five different compositions of each copolymer were prepared so that the reactivity ratios might be determined as described in Chapter 3. After degassing the monomers and the solvent under vacuum in graduated reservoirs, the middle fractions of the monomers and the solvent were distilled into pyrex dilatometers with 10 ml graduated stems containing the required weight of initiator (o.1 % $\frac{W}{V}$), and sealed off under vacuum. The polymerisations were carried out in a thermostat at $60^{o} \pm 0.02^{o}C$ to about 10% conversion for the homopolymers and 5% conversion for the copolymers. The polymers were precipitated three times from chloroform solution by methanol and dried in a vacuum oven for four days at $50^{o}C$. The homopolymers and copolymers were in the form

of white powders except 2,3 - D B P M - M A copolymers with high proportions of M A , P2,3 - D B P A and 2,3 - D B P A copolymers with high concentrations of 2,3 - D B P A which were rubbery in texture.

ii. Preparation of the Blends

Blends of a. P2,3 - D B P M and P M M A; b. P2,3 - D B P A and P M M A; c. P2,3 - D B P M and P M A; d. P2,3 - D B P A and P M A were prepared by dissolving equal amounts of each homopolymer in a small amount of chloroform. The two solutions were then thoroughly mixed and the solvent removed under vacuum leaving a thin film.

2. 4 THERMAL METHODS OF ANALYSIS

i. Thermogravimetric Analysis (T G A)

T G A was carried out on a Du Pont 951 instrument using 5 mg samples and a heating rate of 10^{o}/min from ambient temperature to 500^{o}C in a dynamic atmosphere of nitrogen (50 ml/min).

ii. Differential Scanning Calourmetry (D S C)

D S C curves were obtained using a Du Pont 990 instrument and with the same conditions as for T G A.

iii. Differential Thermal Analysis (D T A)

A Du Pont 900 instrument was used to obtain D T A curves with small glass beads as reference. The sample was heated at 10^{o}/min from ambient temperature to 500^{o}C in a nitrogen flow (80 ml/min).

iv. Thermal Volatilisation Analysis (T V A)

T V A has been used to study the degradation properties of many polymers and is now a well established technique.[6,7] Figure 2.2 shows a schematic diagram of the experimental layout.

The samples are heated on the base of a 6" long glass tube, made from a Pyrex F G 35 flange. The tube is heated in a Perkin-Elmer

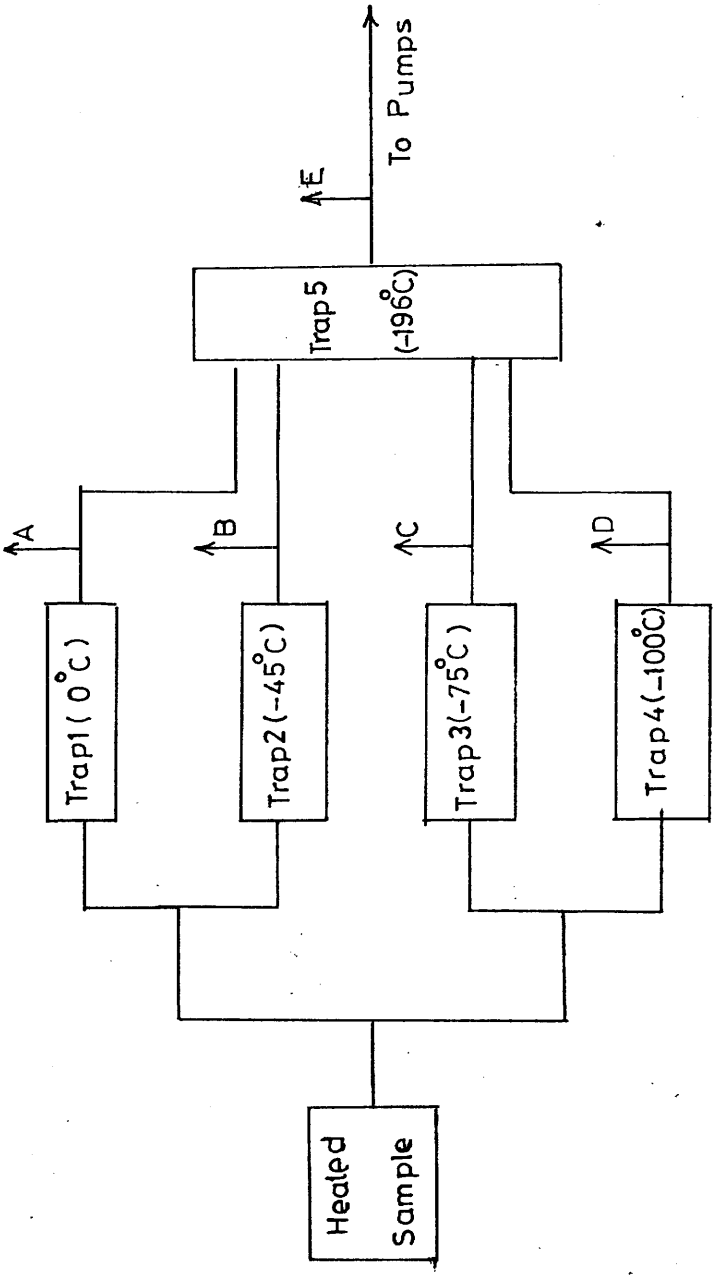


Fig. 2.2. Schematic Layout of Apparatus of T V A

A, B, C, D and E are Pirani gauge heads.

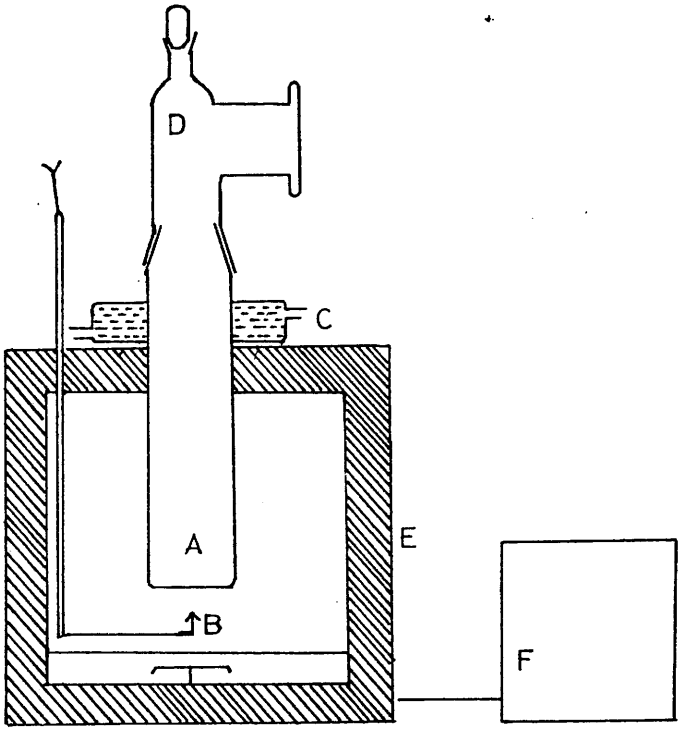


Fig.2.3. T V A Heating Assembly

A : Degradation tube

B : Thermocouple

C : Cooling jacket

D : Removable socket joint

E : Oven

F : Temperature programmer

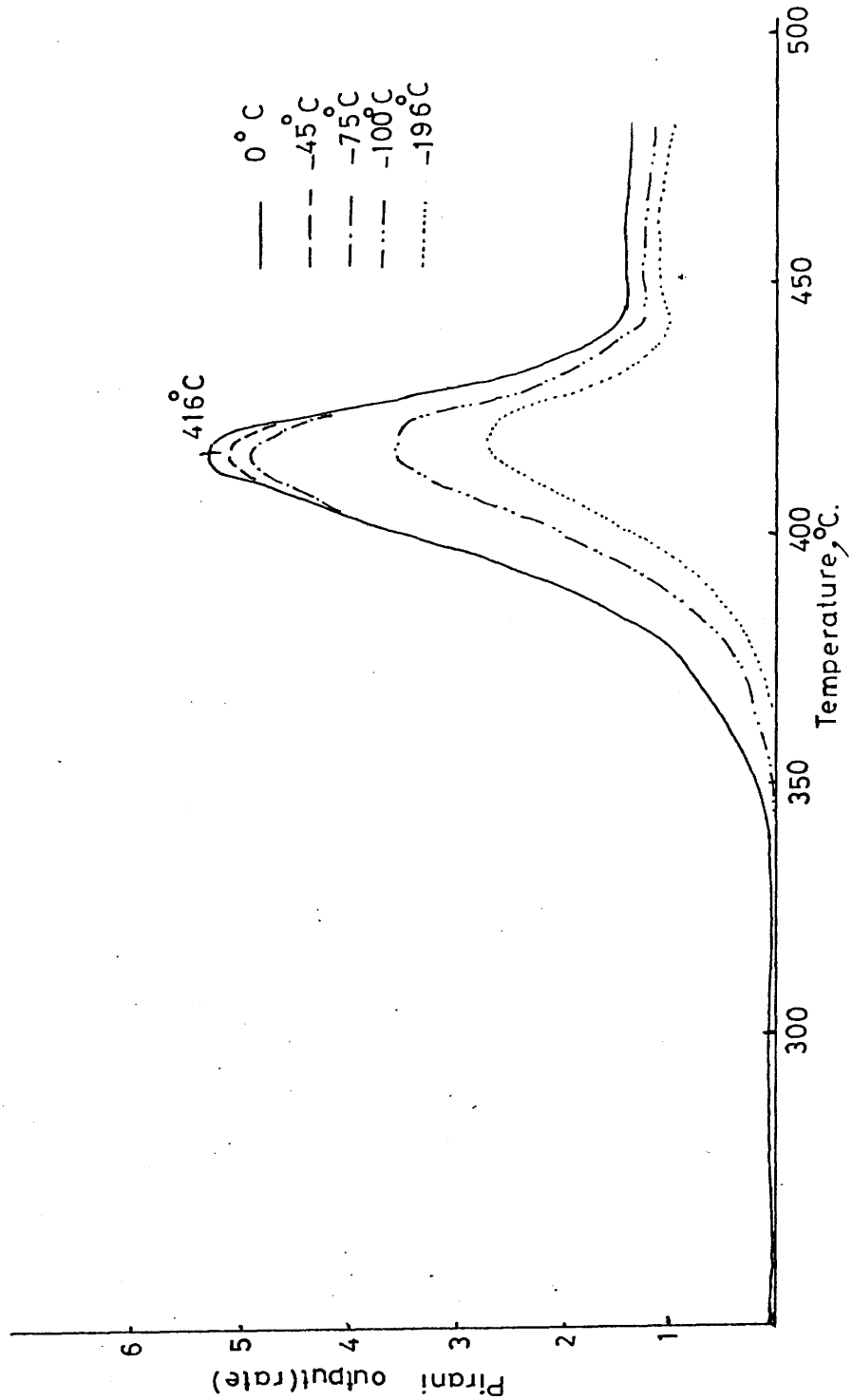


Fig.2. 4. T V A thermogram for P M A, 100 mg , small pieces; heating rate 10^{o}/min.

F 11 Oven, equipped with a linear temperature programmer, at 10^{o}/min from ambient to 500^{o}C, the temperature being measured by a chromel-alumel thermocouple fixed near the base of the tube. Figure 2.3 shows the T V A heating assembly. During the experiment, the top of the tube and the greased flange joints are cooled by a water jacket. The volatile products of degradation pass along four routes (geometrically equivalent) in parallel, each incorporating a trap at a different temperature[8,9] (0^{o}, -45^{o}, -75^{o} and -100^{o}C respectively). The four routes then pass through a common trap at -196^{o}C. Pirani gauges (A - E) are placed after each trap and their outputs, as well as the oven temperature, are fed, via a multihead switch unit into a 12 channel recorder. Pirani gauges A, B, C and D give a non-linear measure of the volatiles which pass through the respective cold traps. Pirani E records the response due to non-condensable gases. The thermogram produced, therefore, is a record of the rate of volatilisation of the polymer sample as a function of temperature. It also gives a preliminary impression of the relative distribution of condensable products from thermal degradation on the basis of their condensability. Figure 2.4 illustrates a thermogram obtained using the T V A technique[10].

v. Thermal volatilisation Analysis at Subambient Temperature (S A T V A)

For any polymer degradation, the products may generally be divided into four fractions:-

a. The involatile residue which remains on the base of the degradation tube. This may usually be analysed by infra-red spectroscopy.

b. The volatile products which do not condense at $-196^{o}C$ (non-condensable). These products can only be collected for identification usually by infra-red spectroscopy or mass spectroscopy after degradation in a closed system.[7]

c. Products volatile only at oven temperature but involatile at ambient temperature. These products condense on the upper parts of the degradation tube (cold ring fractions C R F) and can usually be removed by dissolution with an appropriate solvent for subsequent analysis.

d. Products volatile at ambient temperature but condensed at $-196^{o}C$ (condensable). Subambient T V A (S A T V A) is a technique which has been devised[11,12] to isolate and identify the products in fraction d on the basis of their volatility. The S A T V A equipment is illustrated in figures 2.5 and 2.6.

Thermal degradation is carried out under continuous pumping conditions. After a good vacuum (10^{-5} torr) is achieved with all taps open, trap A is surrounded by liquid nitrogen. The programmed oven temperature (10^{o}/min) is fed, via a multihead switch unit into a 12 channel recorder, the condensable products being retained in trap A. After the required temperature is reached, taps a and c are closed and the liquid nitrogen transferred to tube B into which the condensable products distil. Complete transfer of products from A to B is checked by observing the pressure in Piranis 1 and 2. Tap b is then closed and tap c opened to the pumps. By removing liquid nitrogen from tube B the products are allowed to distil slowly into trap C which is surrounded by liquid nitrogen. As each product distils, Pirani 2 measures a change in the pressure which is displayed as a series of peaks on the recorder depending upon the volatility of

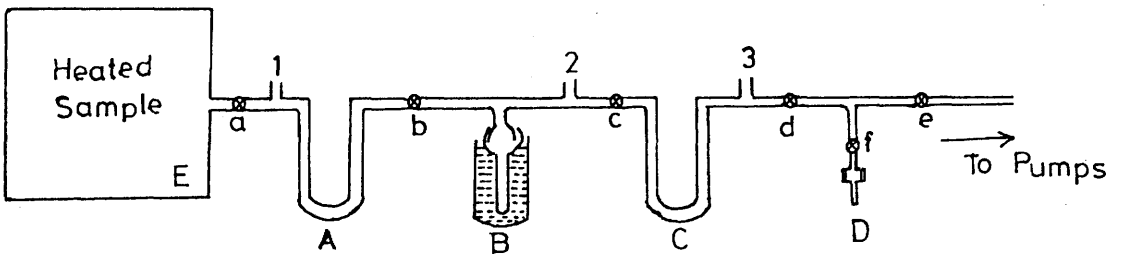


Fig.2.5. Subambient T V A Apparatus

1,2 and 3 Pirani gauges

A and C U traps

B Tube surrounded by benzene or p-xylene

D Gas cell or cold finger

E Heating system as shown in figure 2.3

a, b, c, d, e and f Stopcocks

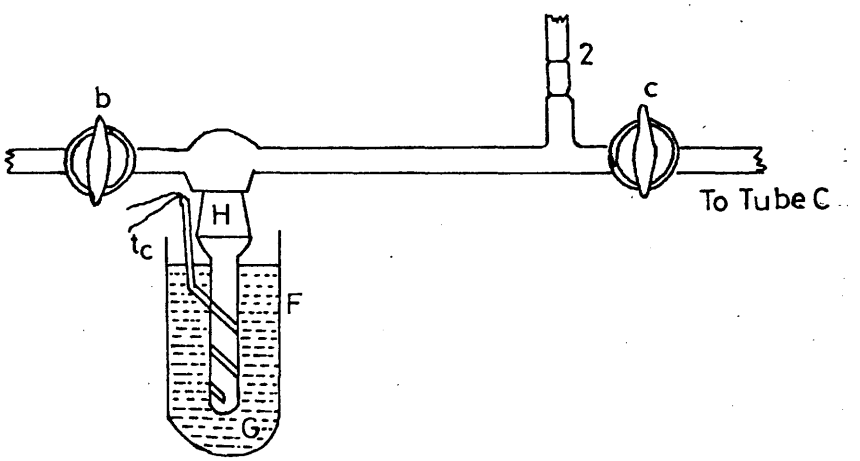


Fig. 2.6. Details of tube B shown in figure 2.5 for subambient T V A apparatus

t_c Chromel alumel thermocouple leads

F Pyrex glass round bottomed tube

G Benzene or p-xylene

H Sample tube with 34 joint

the various condensable products. It is easy to separate the products in each peak for qualitative or quantitative analysis by surrounding tube B with liquid nitrogen and closing taps c and e. The products are allowed to condense in the gas cell or in the cold finger D which is surrounded with liquid nitrogen, by removing the liquid nitrogen from trap C and observing the pressure in Pirani 3. In this way identification of all condensable degradation products may be achieved.

2. 5 ANALYTICAL TECHNIQUES

i. Infra-red Spectroscopy (I R)

Spectra were recorded on a Perkin-Elmer 257 grating spectrometer, for either qualitative or quantitative measurement. Polymer samples were examined in the form of KBr discs, in solution using NaCl cells or as films cast on NaCl plates. Cold ring fractions were run in solution using $CHCl_3$ as solvent. Residues were run in the form of KBr discs. Condensable products were recorded as liquids between salt plates or in the gas phase using small gas cells with NaCl windows (15 mm). Non-condensable products were recorded in the gas phase. Infra-red spectroscopy was also used for quantitative measurement of the gaseous degradation products, namely, hydrogen bromide, carbon dioxide, propene, methyl bromide, allyl bromide and methanol. The technique used for this is shown in figure 2.7 using reference gases. By changing the pressure in the gas cell, which can be measured by mercury monometer, different ir peak heights can be obtained. From the conversion of transmittance to absorbance of an appropriate peak of each compound, the optical density can be calculated. Figures 2.8 and 2.9 show the optical density vs pressure

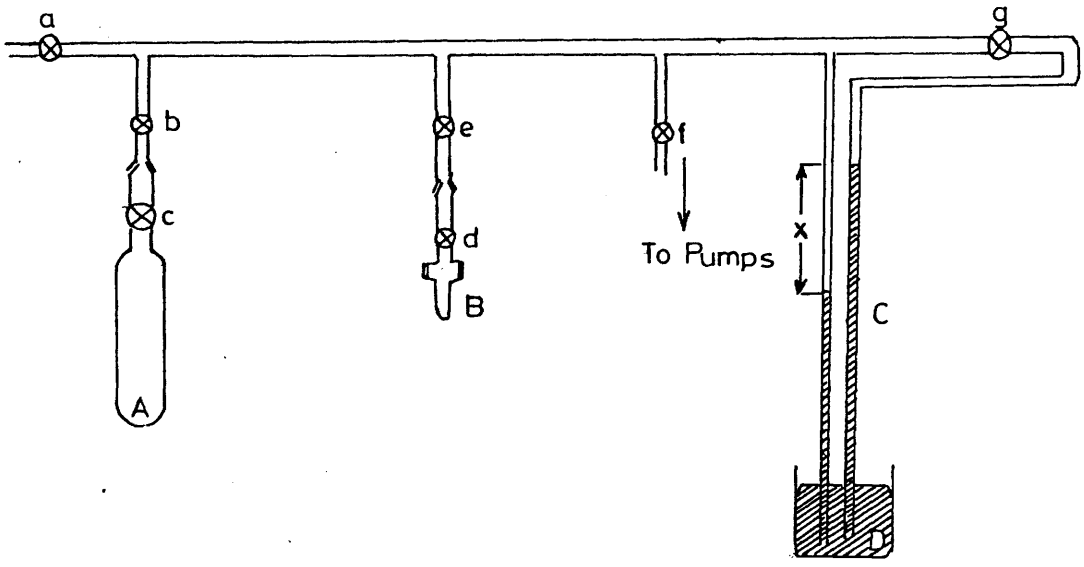


Fig.2.7. Apparatus employed for calibration of gas cell

A : Reference gas reservoir

B : I r gas cell

C : Mercury filled monometer tubes of same bore

D : Mercury reservoir

a, b, c, d, e, f and g Stopcocks

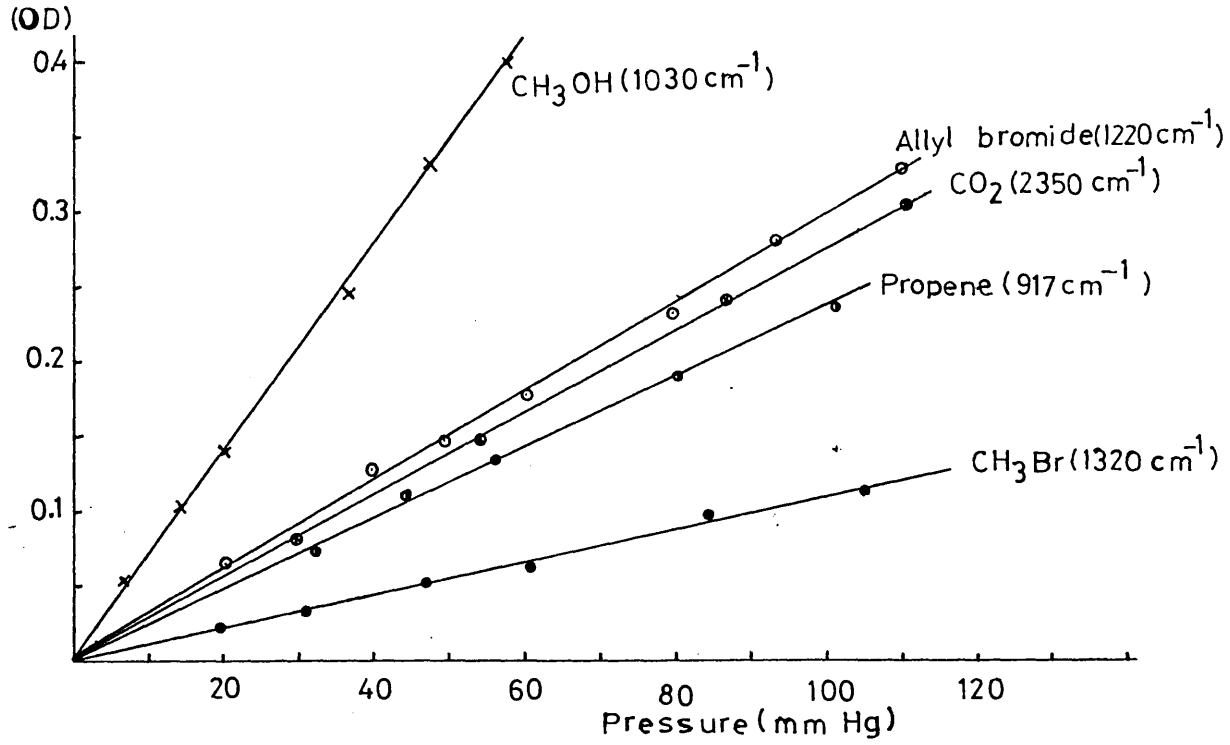


Fig.2.8. I r calibration plot of some pure materials.

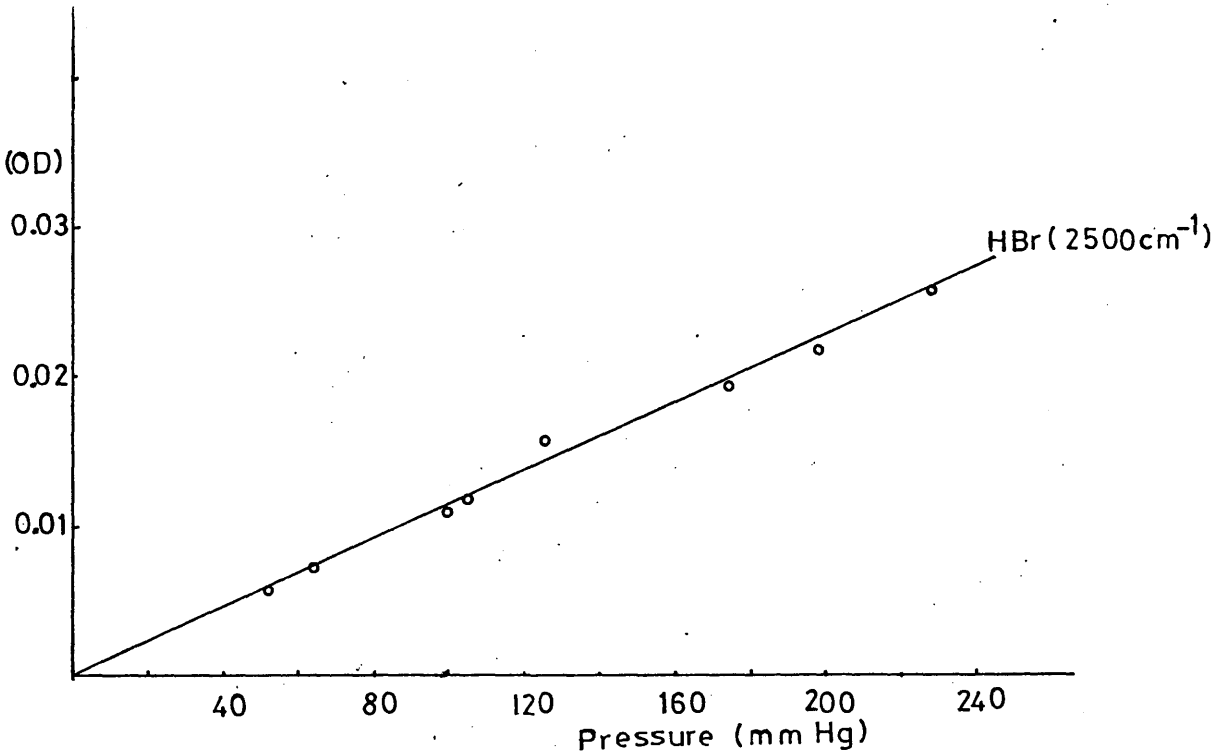


Fig.2.9. I r calibration plot of HBr.

(mm Hg) relationship of the reference compounds. Knowing the volume of the gas cell, the amount of each compound (in moles) can be calculated from the gas equation :

$$P V = nR T$$

where P : the pressure of the compounds (mm Hg), V : volume of gas cell (ml), n : number of moles of each compound, R : gas constant (ml cm Hg $mole^{-1}K$) and T : temperature (K).

ii. Mass Spectroscopy

An EI MS 12 was used to assist identification of the condensable and non-condensable degradation products.

iii. Nuclear Magnetic Resonance Spectroscopy (N M R)

Spectra were obtained from a Perkin-Elmer R32 90 M Hz Spectrometer using $CDCl_3$ or CCl_4 as solvent. Ten integrals were taken for the determination of copolymer compositions.

iv. Microanalysis

Bromine contents were estimated using a potontiometric titration method introduced by Cheng[13]. Three values of bromine content for each copolymer were taken to give a mean value for the calculation of copolymer compositions.

v. Molecular Weight Measurement

Number Average Molecular Weights of the polymers were measured on a Hewlett-Packard 501 High Speed Membrane Osmometer with cellophane 300 membrane and using toluene as solvent.

vi. Gas-Liquid Chromatography (g l c)

A Perkin-Elmer F11 g l c with flame ionization analyser was used for quantitative measurements of the condensable and cold ring fractions of degradation products using a suitable internal standard. A series of pure samples of each product were mixed with a known amount of the

internal standard, 1 ml of anhydrous diethyl ether, and run on the chromatograph. A list of the columns employed and the conditions under which they were used is given in Table 2.1.

Table 2. 1. G L C Columns used for Investigation of Degradation Products

Column	Programme	Use
5 ft. ¼ inch diameter 10% microwax on chromosorb	isothermal at 90°C	liquid volatiles & some monomers
"	isothermal at 140°C	liquid volatiles, short chain fragment and some monomers
10 ft. ¼ inch diameter 1% OV1 on chromosorb	isothermal at 250°C	cold ring fractions

The internal standard used in this study was 2-bromoethyl methacrylate (2 - B E M).

The carrier gas was nitrogen at a flow rate 20 ml/min.

Figures 2.10 and 2.11 show calibration curves of some pure materials with the internal standard.

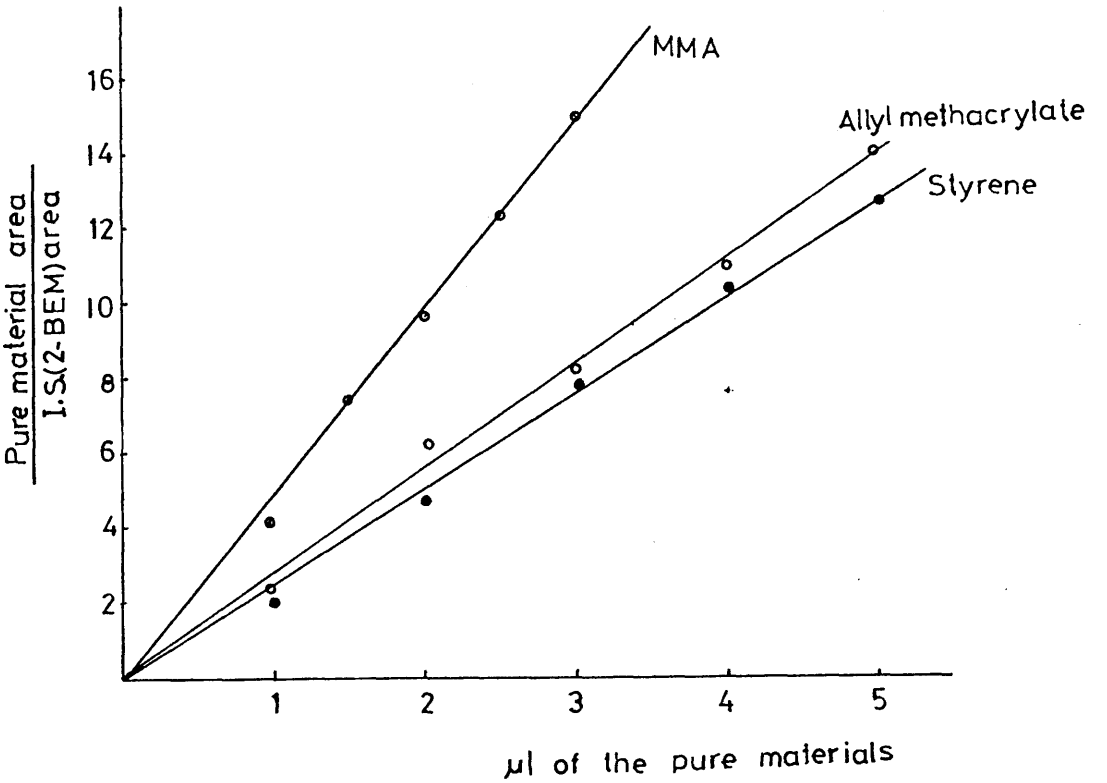


Fig. 2.10. G L C calibration plot of some pure materials using 2 - B E M as internal standard.

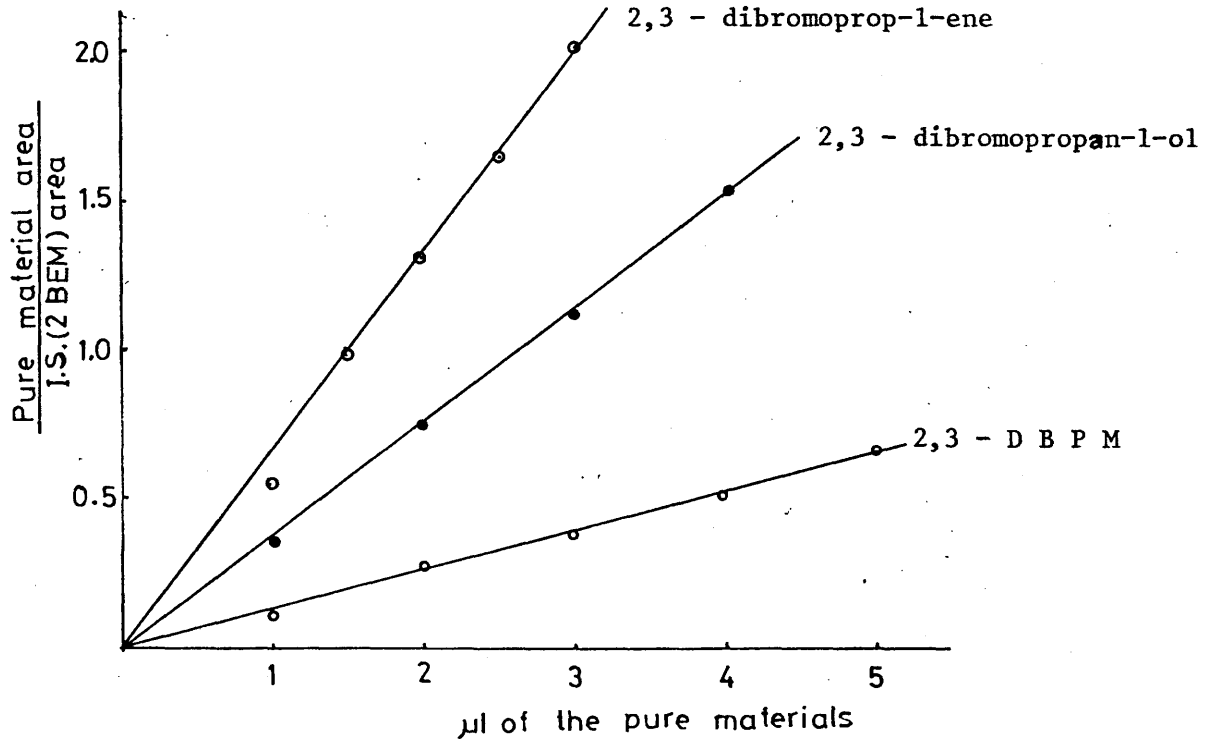


Fig. 2.11. G L C calibration Plot of some pure materials using 2 - B E M as internal standard.

CHAPTER 3

DETERMINATION OF REACTIVITY RATIOS

3.1 INTRODUCTION

The reactivity ratios for 2,3- D B P M and 2,3- D B P A with other monomers have not been previously reported. The usual method of determination of reactivity ratios involves polymerising a variety of feed compositions to low conversion. The copolymers are isolated and their compositions measured. Two methods of analysis of the copolymers were found to be appropriate, namely, Microanalysis and Nuclear Magnetic Resonance Spectroscopy.

3.2 MICROANALYSIS

20 mg samples of the copolymers are sufficient for estimating bromine contents using the potentiometric titration method introduced by Cheng.[13] Figures 3.1 to 3.6 show the theoretical monomer compositions of the copolymers plotted against the corresponding percentage bromine values. Percentage bromine data from microanalysis can then be inserted on the curves and the corresponding molar ratio read off from the abscissa. Table 3.1 shows the molar ratios $\frac{M1}{M2}$ in the copolymers obtained by this method.

3.3 NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance spectra were obtained using a Perkin-Elmer R32 90 M Hz Spectrometer with integrator, using 20 mg samples of copolymers. The copolymers 2,3- D B P M-S and 2,3- D B P A-S, were dissolved in 1 ml of CCl_4. All other copolymers were dissolved in 1 ml of C D Cl_3. Ten integrals were obtained for each sample and the average used for the calculation of copolymer compositions. The monomer compositions of the copolymer

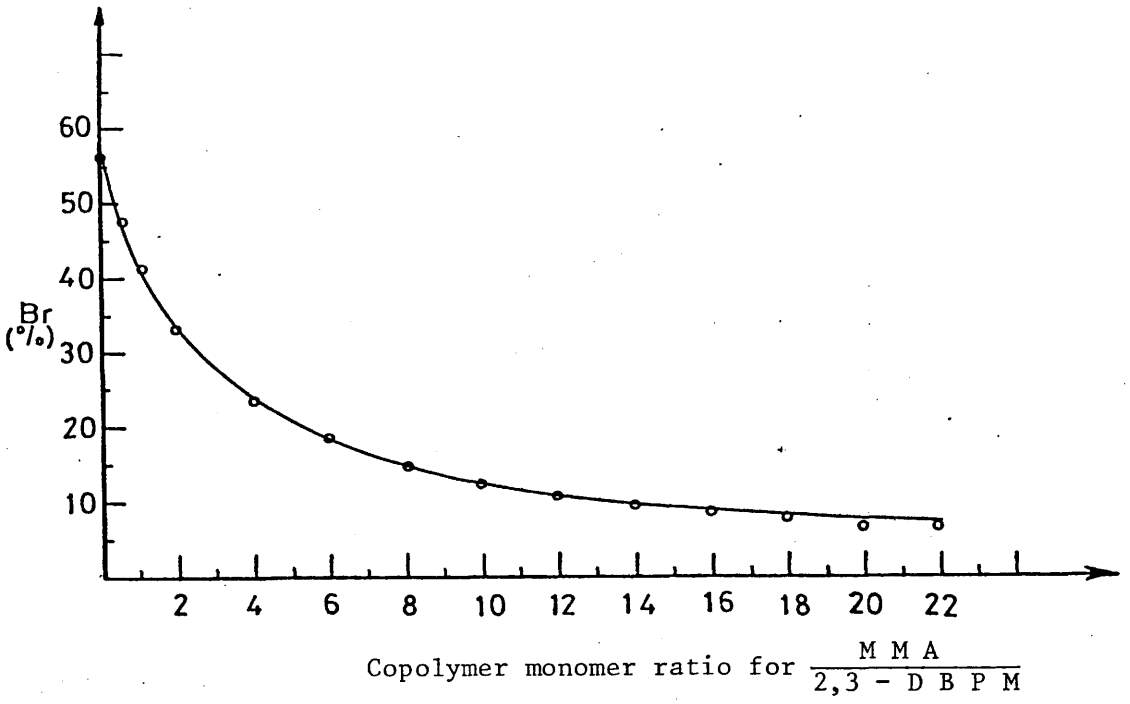


Fig.3.1. Theoretical curve of bromine content V S copolymer monomer ratio for $\frac{MMA}{2,3 - D\ B\ P\ M}$ copolymers.

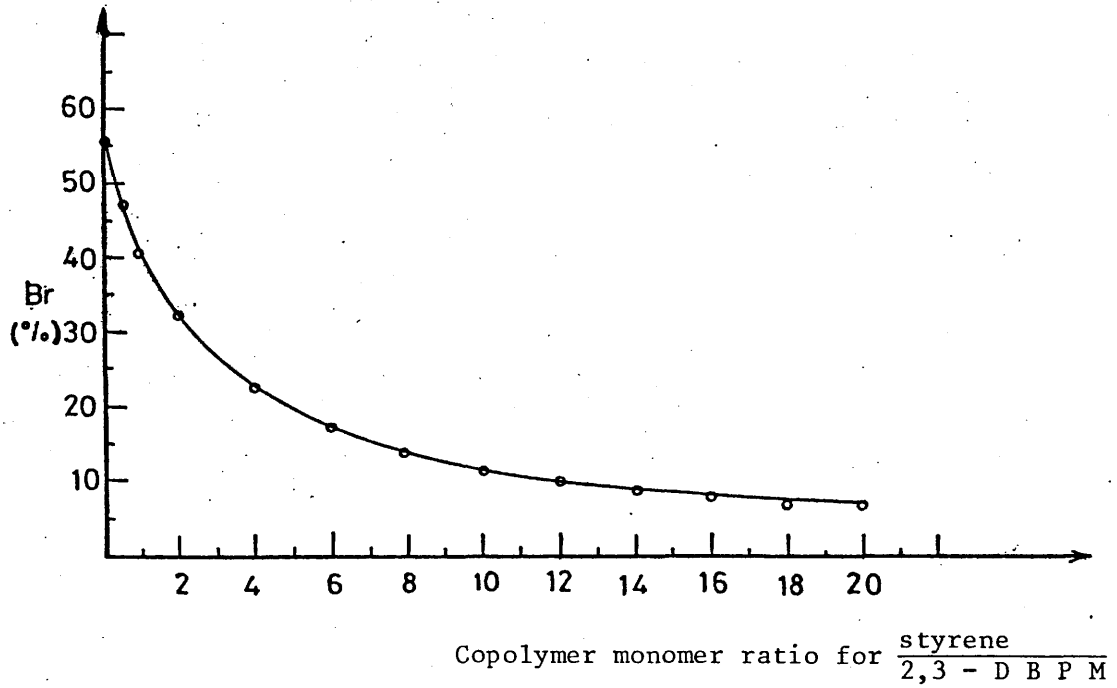


Fig.3.2. Theoretical curve of bromine content V S copolymer monomer ratio for $\frac{\text{styrene}}{2,3 - D\ B\ P\ M}$ copolymers.

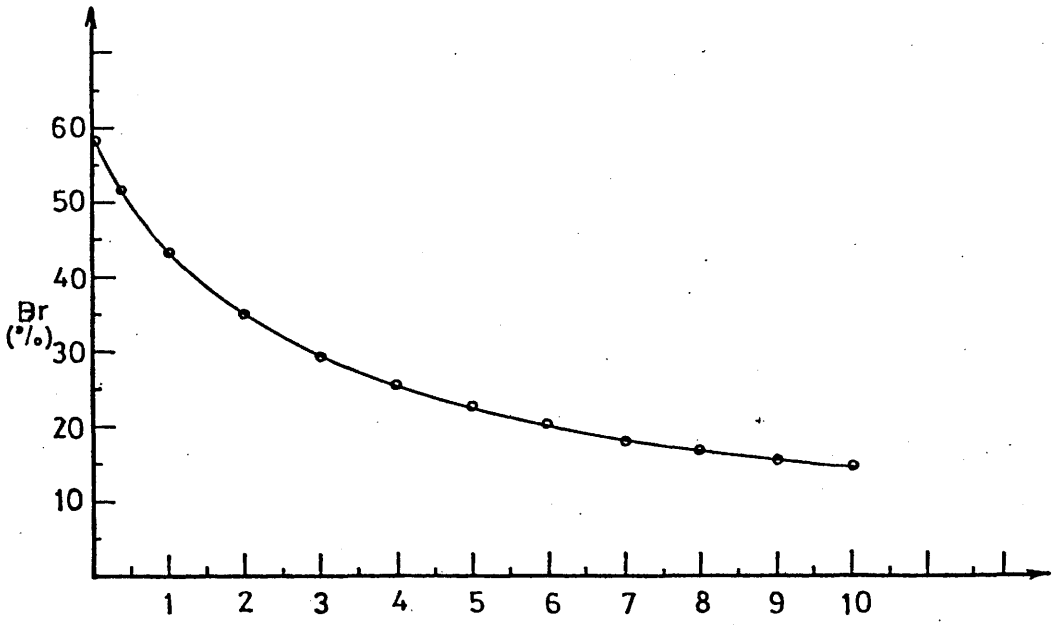


Fig.3.3. Theoretical curve of bromine content V S copolymer monomer ratio for $\frac{M\ A}{2,3 - D\ B\ P\ M}$.

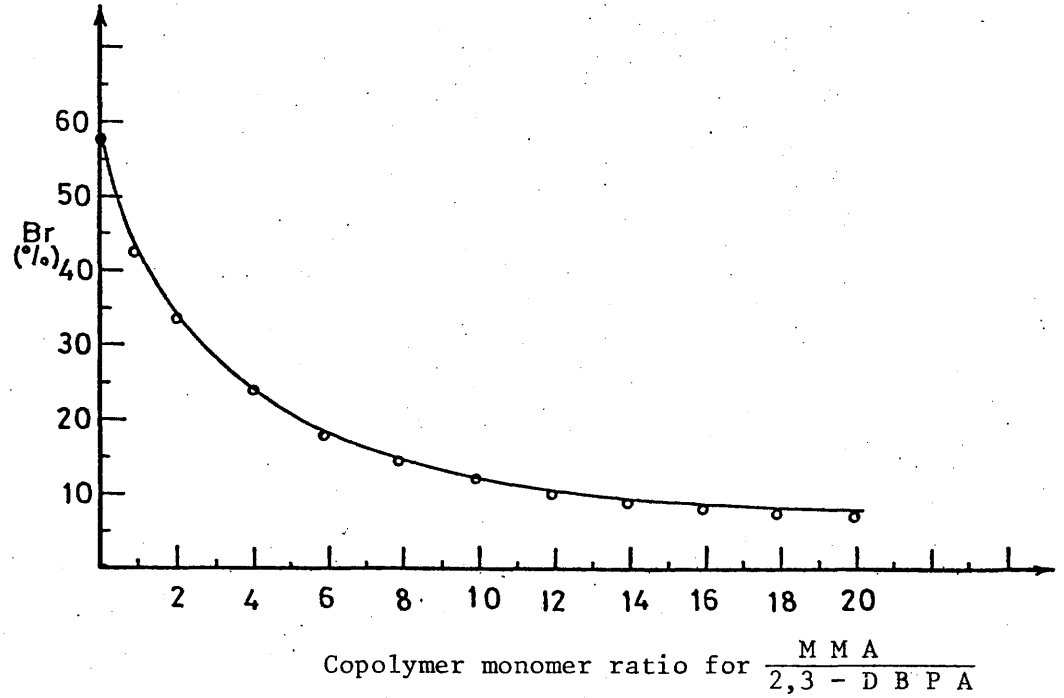


Fig.3.4. Theoretical curve of bromine content V S copolymer monomer ratio for $\frac{M\ M\ A}{2,3 - D\ B\ P\ A}$.

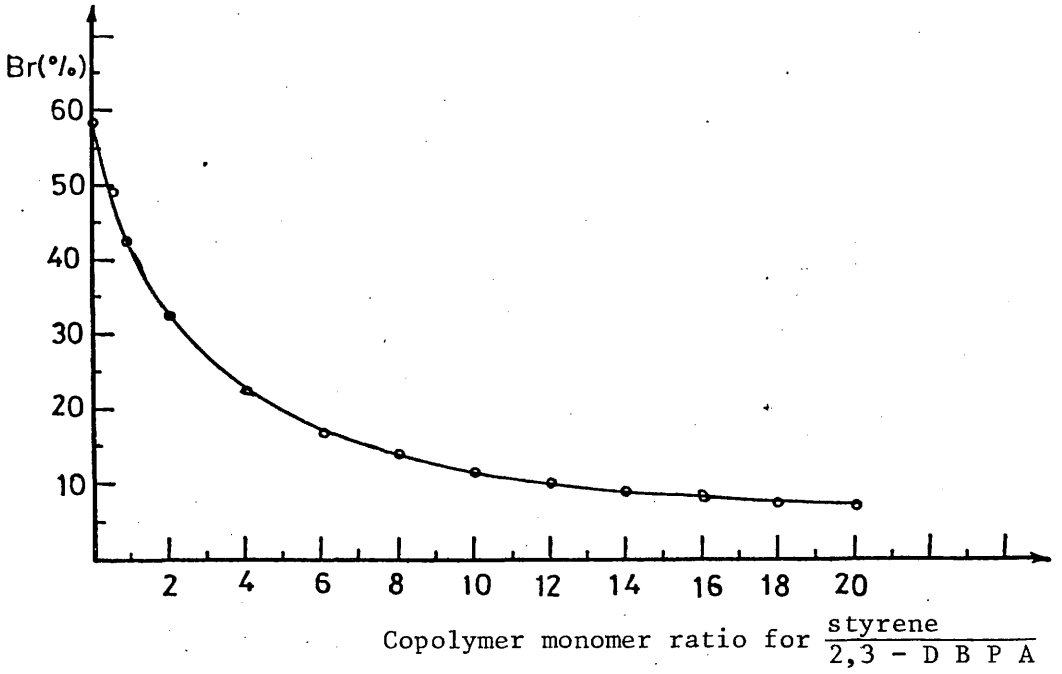


Fig.3.5. Theoretical curve of bromine content V S copolymer monomer ratio for $\frac{\text{styrene}}{\text{2,3 - D B P A}}$.

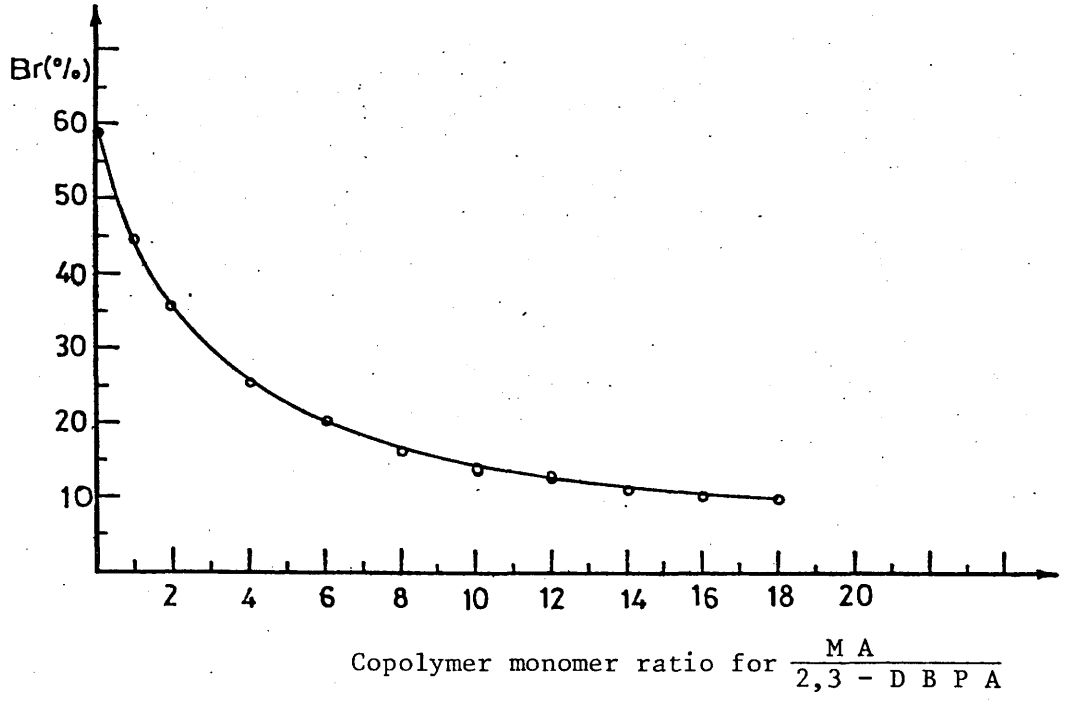


Fig.3.6. Theoretical curve of bromine content V S copolymer monomer ratio for $\frac{\text{M A}}{\text{2,3 - D B P A}}$.

may be calculated from the ratios of these integrals which are proportional to the number of protons contributing to the peaks. This method has previously been used to determine the monomer contents in vinyl acetate - ethylene copolymers[14,15] but reactivity ratios were not calculated. It has also been used previously to determine the reactivity ratios for the styrene - M M A[16] and methacrylate - acrylate copolymers[17]. Figures 3.7 and 3.8 show the nmr spectra of 2,3 - D B P M - M M A and 2,3 - D B P M - S copolymers respectively. In figure 3.7, peak A at 4.35 is due to $-OCH_2CHBr$ - protons of 2,3 - D B P M or 2,3 - D B P A. Peak B at 3.65 is a composite peak, due to $-OCH_3$ protons of the M M A or M A unit and $-CH_2Br$ protons of the 2,3 - D B P M or 2,3 - D B P A group. The integral due to the $-OCH_3$ protons may be calculated by multiplying the integral value of peak A by $\frac{2}{3}$ and substracting the results from the total integral due to peak B.

Hence,

I $-OCH_2CHBr$ - $\propto$ 3 (number of 2,3 - D B P M or 2,3 - D B P A units in the chain), and

I $-OCH_3$ $\propto$ 3 (number of M M A or M A in the chain)

Then,

$$\text{The molar ratio } \frac{M_1}{M_2} \text{ in the copolymer} = \frac{\text{I } -OCH_2CHBr-}{\text{I } -OCH_3}$$

In figure 3.8 peak A at 7.12 is due to the five protons in styrene. Peaks B and C at 4.35 and 3.85 are due to $-OCH_2-CHBr$ and $-CH_2Br$ respectively. The integral value due to peaks A and B + C can easily be estimated.

Hence,

I $-OCH_2-CHBr$ - + $-CH_2Br$ $\propto$ 5 (number of 2,3 - D B P M or 2,3 -

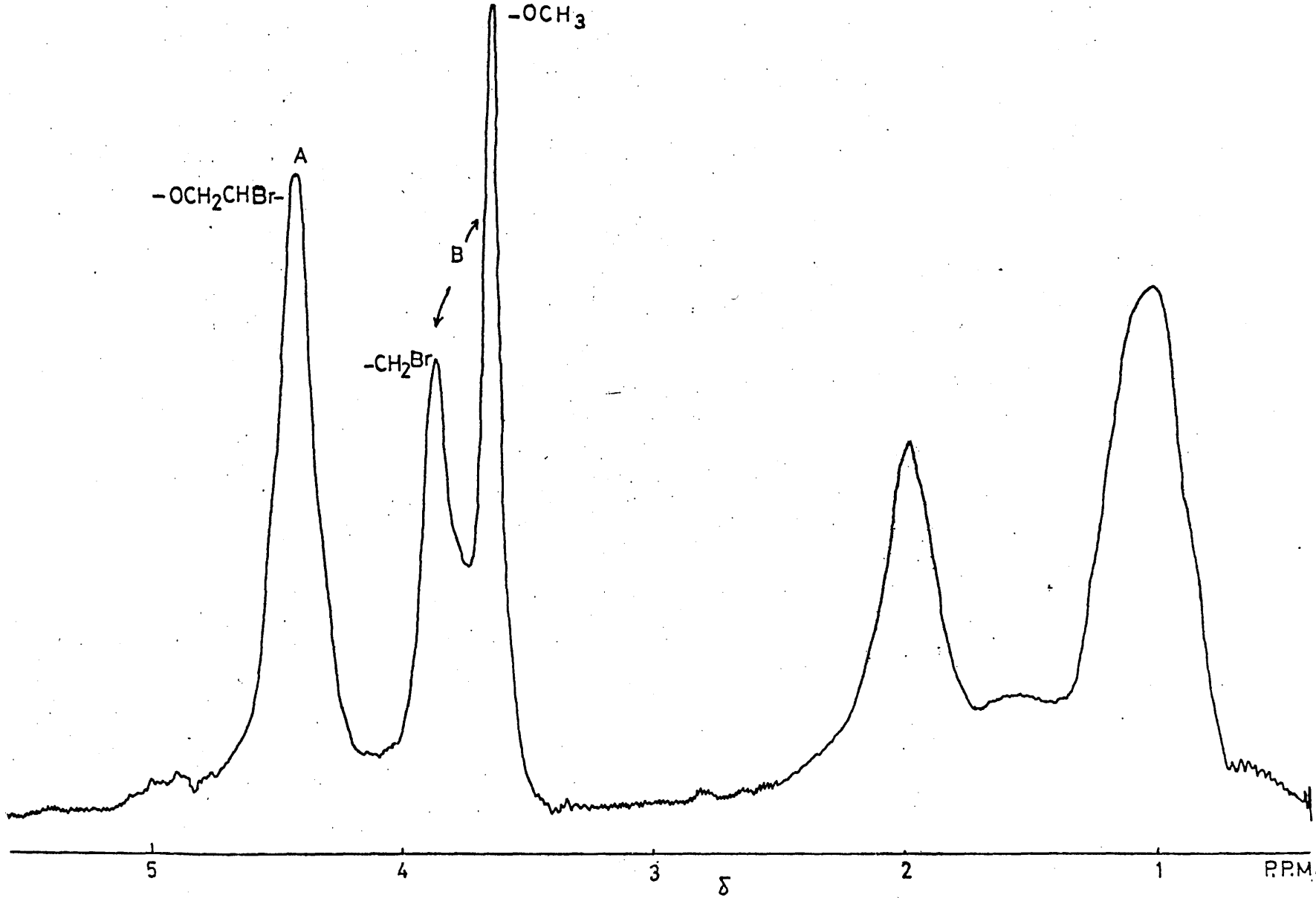


Fig. 3.7. Nuclear Magnetic Resonance Spectrum of 2,3 - D B P M - M M A copolymer.

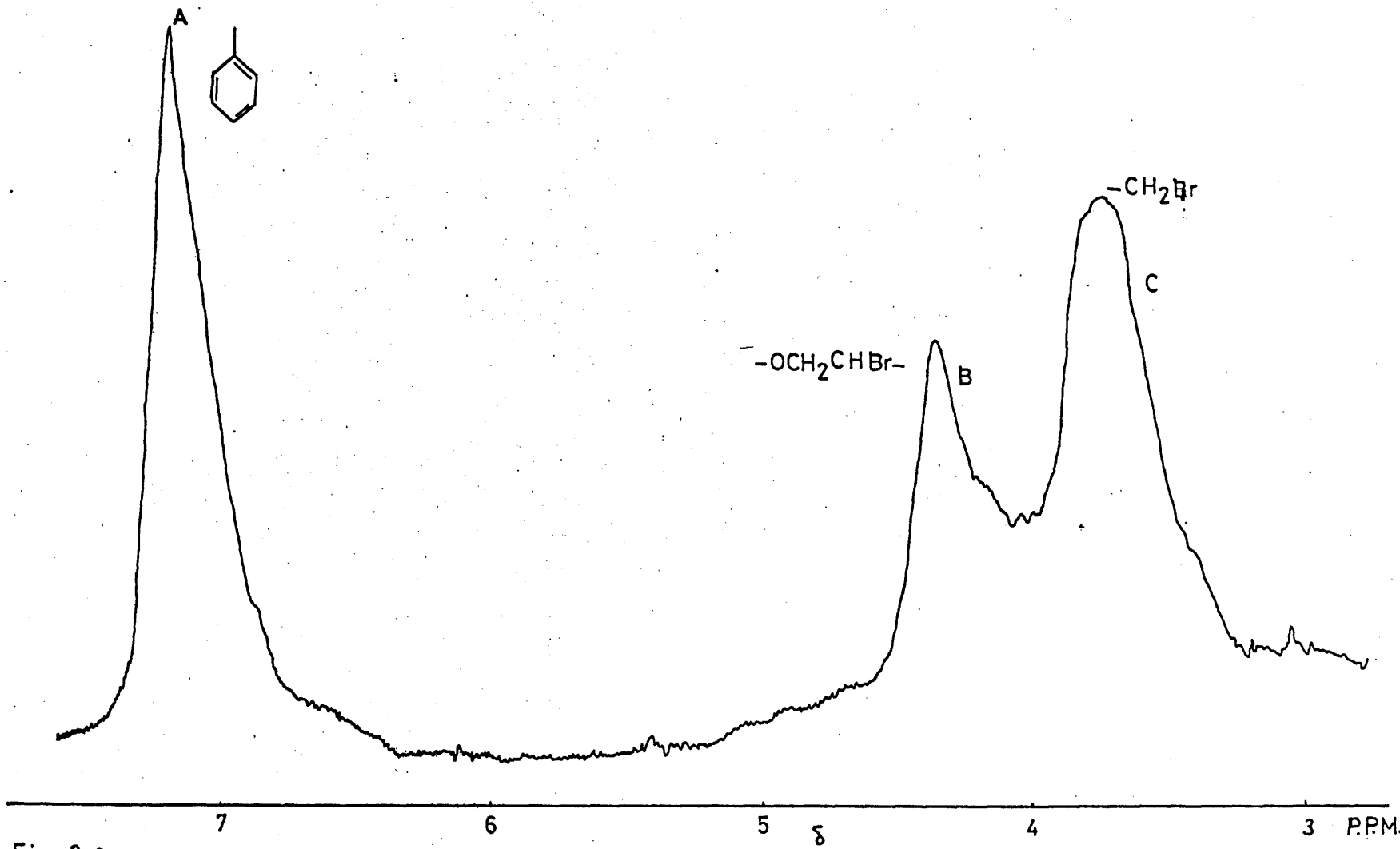
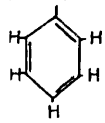
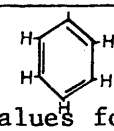


Fig.3.8. Nuclear Magnetic Resonance Spectrum of 2,3 - D B P M - S copolymer.

D B P A units in the chain)

and I  $\propto$ 5 (number of styrene units in the chain)

Then,

The molar ratio in the copolymer $\frac{M_1}{M_2} = \frac{I\ -OCH_2CHBr- + I\ -CH_2Br}{I\ \text{  }}$

The ratios obtained by the above method gave the values for the copolymer compositions shown in table 3. 2.

Table 3 . 1. Copolymer Compositions from Bromine Analysis

Monomer pair M_1	M_2	Monomer mixture: Number of moles of M_1 (n_1)	Monomer mixture: Number of moles of M_2 (n_2)	% Bromine content	Molar ratio in copolymer $\frac{M_1}{M_2}$
2,3 - D B P M	M M A	0.006	0.198	6.8	0.04
		0.012	0.189	10.34	0.08
		0.045	0.167	25.4	0.30
		0.102	0.054	44.48	1.32
		0.114	0.034	49.00	2.37
2,3 - D B P M	S	0.012	0.183	16.74	0.16
		0.030	0.191	24.37	0.31
		0.041	0.174	31.40	0.47
		0.095	0.061	45.00	1.43
		0.100	0.061	46.10	1.53
2,3 - D B P M	M A	0.012	0.210	23.61	0.22
		0.024	0.210	31.00	0.38
		0.047	0.166	43.3	1.05
		0.089	0.110	49.55	2.38
		0.13	0.088	52.62	4.80

Cont'd Table 3. 1. Copolymer Compositions from Bromine Analysis

Monomer pair M_1	M_2	Monomer mixture: Number of moles of M_1 (n_1)	Monomer mixture: Number of moles of M_2 (n_2)	% Bromine content	Molar ratio in copolymer $\frac{M_1}{M_2}$
2,3 - D B P A	MMA	0.026	0.234	12.25	0.098
		0.032	0.180	18.00	0.164
		0.039	0.153	22.20	0.222
		0.097	0.090	39.35	0.714
		0.116	0.045	46.12	1.429
2,3 - D B P A	S	0.026	0.226	20.83	0.204
		0.032	0.174	24.02	0.264
		0.045	0.148	31.28	0.417
		0.097	0.087	41.04	0.909
		0.116	0.044	46.03	1.333
2,3 - D B P A	M A	0.013	0.254	14.17	0.098
		0.019	0.221	20.31	0.169
		0.064	0.221	33.28	0.431
		0.075	0.110	41.17	0.741
		0.102	0.099	45.91	1.053

Table 3 . 2. Copolymer Compositions from Nuclear Magnetic Resonance Analysis

Monomer pair M_1	M_2	Number of moles of M_1 (n_1)	Number of moles of M_2 (n_2)	Molar ratio in copolymer $\frac{M_1}{M_2}$
2, 3 - D B P M	M M A	0.006	0.198	0.048
		0.012	0.189	0.095
		0.045	0.167	0.329
		0.102	0.054	1.730
		0.114	0.034	2.475
2, 3 - D B P M	S	0.012	0.183	0.157
		0.030	0.191	0.313
		0.041	0.174	0.465
		0.095	0.061	1.449
		0.100	0.061	1.515
2, 3 - D B P M	M A	0.012	0.210	0.221
		0.024	0.210	0.391
		0.047	0.166	1.085
		0.089	0.110	2.381
		0.13	0.088	4.630

Cont'd Table 3. 2. Copolymer Compositions from Nuclear Magnetic Resonance Analysis

Monomer pair M_1	M_2	Number of moles of M_1 (n_1)	Number of moles of M_2 (n_2)	Molar ratio in copolymer $\frac{M_1}{M_2}$
2,3 - D B P A	M M A	0.026	0.234	0.097
		0.032	0.180	0.167
		0.039	0.153	0.225
		0.097	0.090	0.732
		0.116	0.045	1.227
2,3 - D B P A	S	0.026	0.226	0.195
		0.032	0.174	0.295
		0.045	0.148	0.404
		0.097	0.087	0.782
		0.116	0.044	1.227
2,3 - D B P A	M A	0.013	0.254	0.099
		0.019	0.221	0.164
		0.064	0.221	0.403
		0.075	0.110	0.800
		0.102	0.099	0.954

From the values of n_1, n_2 and the molar ratios $\frac{M_1}{M_2}$ in the copolymer shown in Tables 3.1 and 3.2 reactivity ratios were calculated by using the equation[18]

$$\frac{f_1 (1 - 2F_1)}{(1 - f_1) F_1} = \frac{f_1^2 (F_1 - 1)}{(1 - f_1)^2 F_1} r_1 + r_2$$

where $F_1 = \frac{M_1 / M_2}{M_1 / M_2 + 1}$ (mole fraction of M_1 in polymer)

$$f_1 = \frac{n_1}{n_1 + n_2}$$ (mole fraction of M_1 in feed)

and r_1 and r_2 are the reactivity ratios for the copolymerisation of 2,3-D B P M or 2,3-D B P A with MMA, Styrene or MA respectively.

Plots of $\frac{f_1 (1 - 2F_1)}{(1 - f_1) F_1}$ versus $\frac{f_1^2 (F_1 - 1)}{(1 - f_1)^2 F_1}$ Figures 3. 9, 3. 11, 3. 13, 3. 15, 3. 17 and 3. 19 and of

$\frac{f_2 (1 - 2F_2)}{(1 - f_2) F_2}$ versus $\frac{f_2^2 (F_2 - 1)}{(1 - f_2)^2 F_2}$ in figures 3. 10, 3. 12, 3. 14, 3. 16, 3. 18 and 3. 20 where,

$F_2 = \frac{M_2 / M_1}{M_2 / M_1 + 1}$ (mole fraction of M_2 in polymer)

and $f_2 = \frac{n_2}{n_1 + n_2}$ (mole fraction of M_2 in feed)

From the slopes and intercepts reactivity ratio values may be obtained as shown in Table 3. 3.

Thus, microanalysis and nuclear magnetic resonance can lead to values of reactivity ratios for these copolymer systems which are in good agreement.

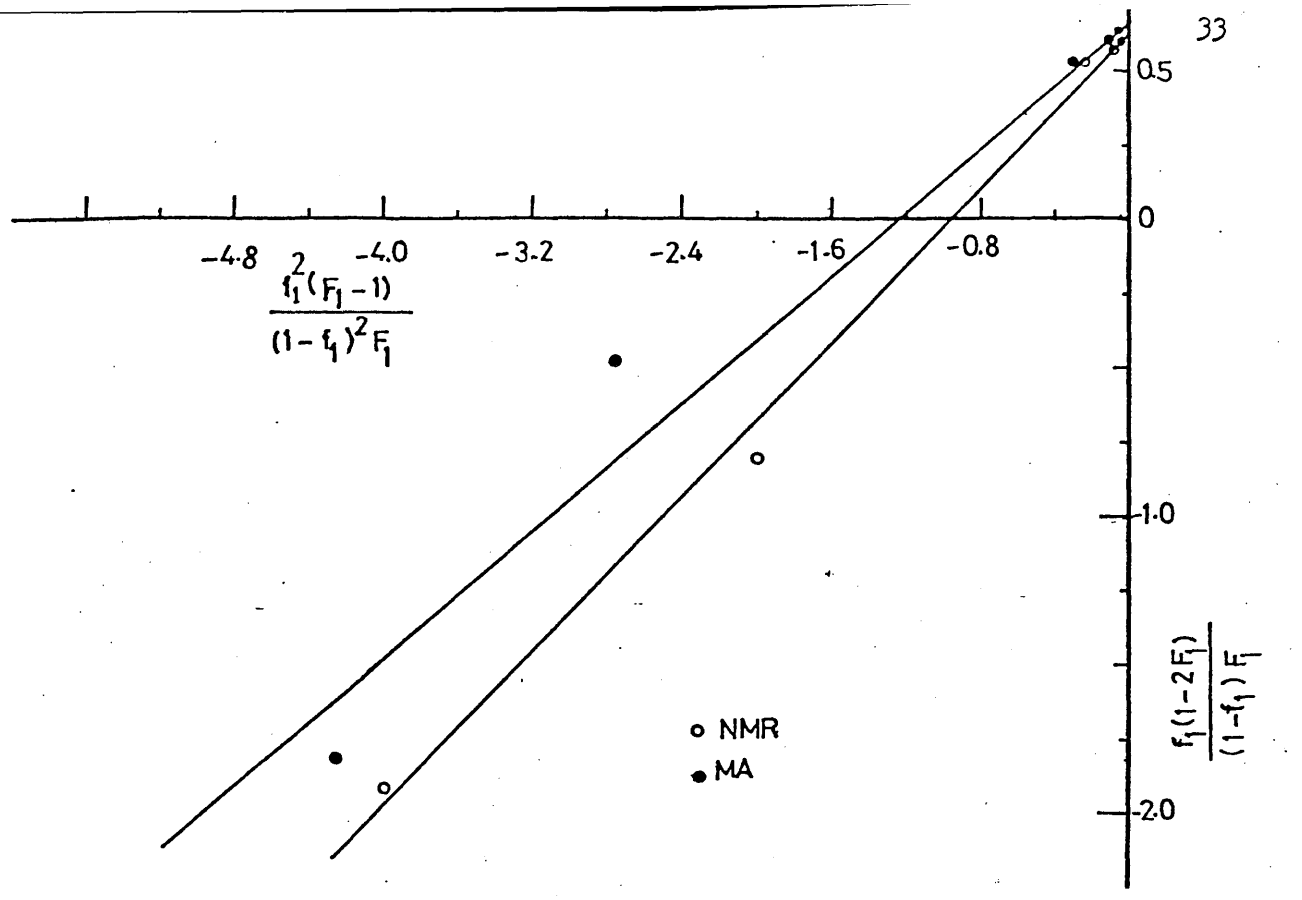


Fig.3.9. Graph of $\frac{f_1^2\ (F_1-1)}{(1-f_1)^2\ F_1}$ versus $\frac{f_1\ (1-2F_1)}{(1-f_1)\ F_1}$ for

2,3 - D B P M - M M A copolymers.

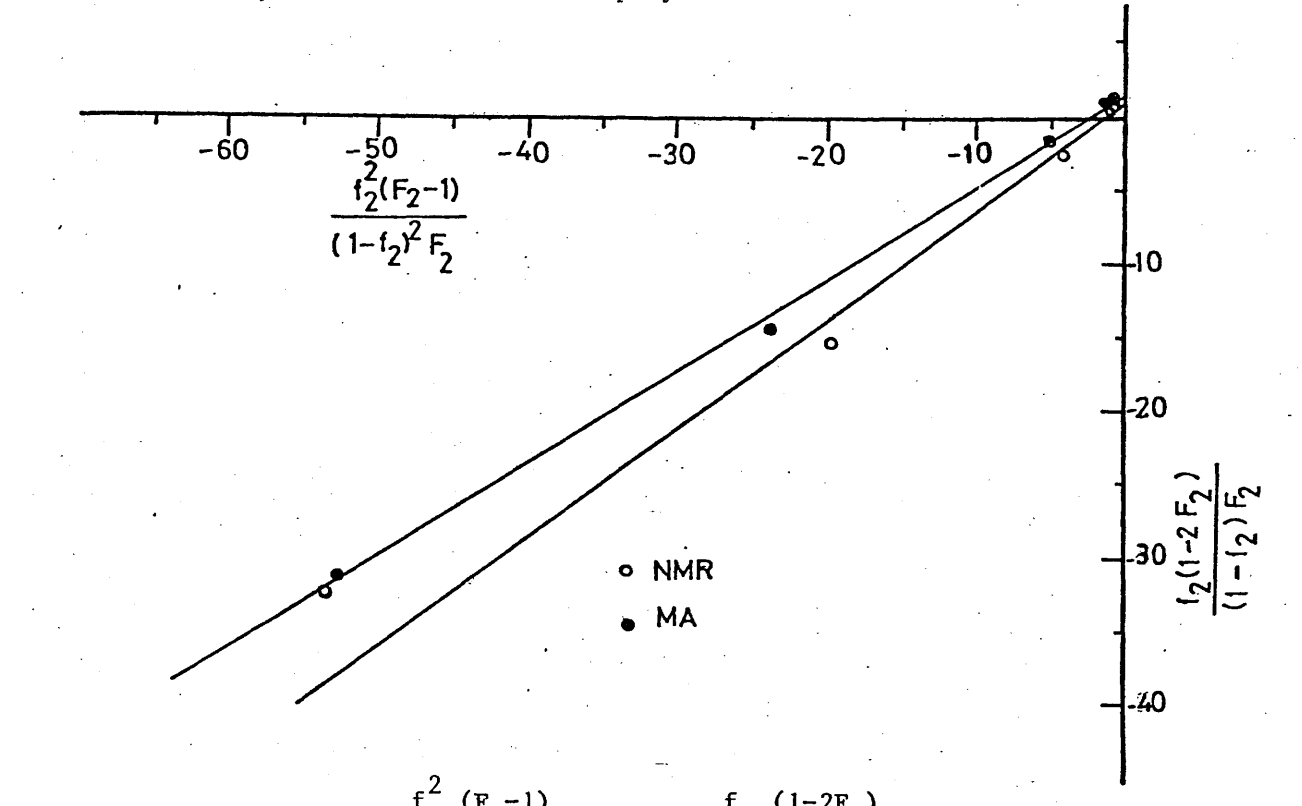


Fig. 3.10. Graph of $\frac{f_2^2\ (F_2-1)}{(1-f_2)^2\ F_2}$ versus $\frac{f_2\ (1-2F_2)}{(1-f_2)\ F_2}$ for

2,3 - D B P M - M M A copolymers.

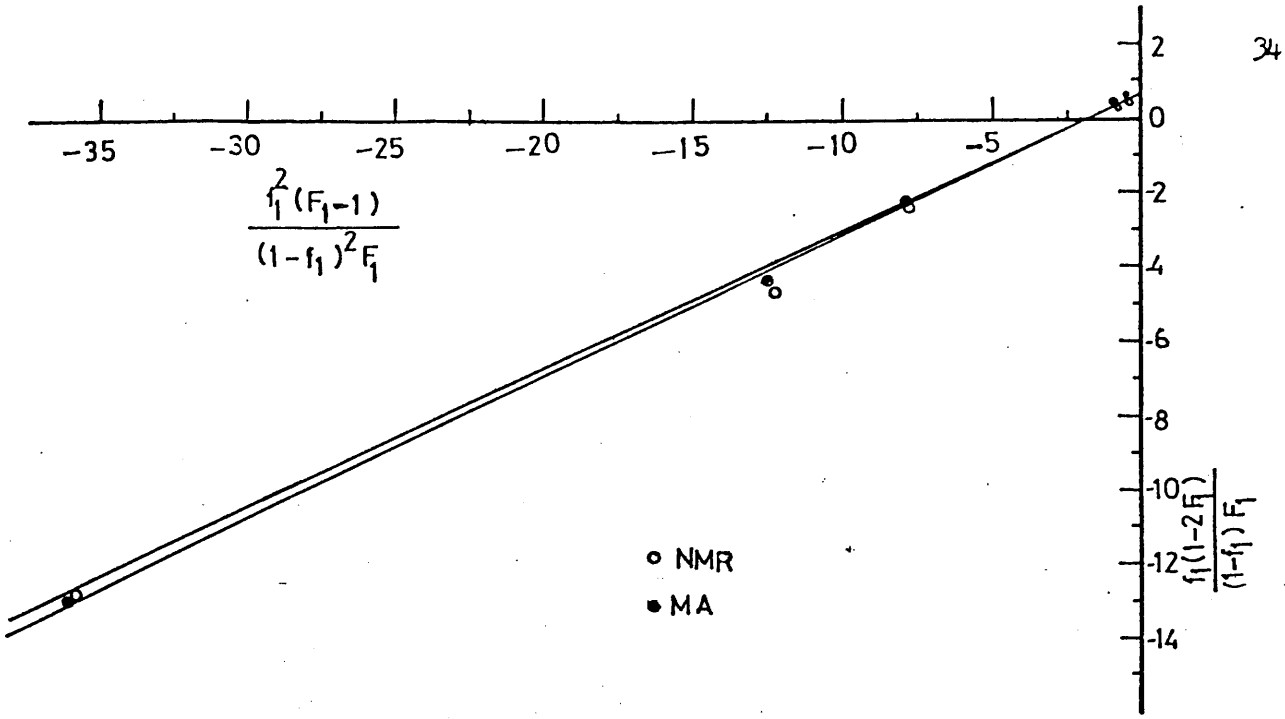


Fig.3.11. Graph of $\frac{f_1^2\ (F_1-1)}{(1-f_1)^2\ F_1}$ versus $\frac{f_1\ (1-2F_1)}{(1-f_1)\ F_1}$ for

2,3 - D B P M - Styrene copolymers.

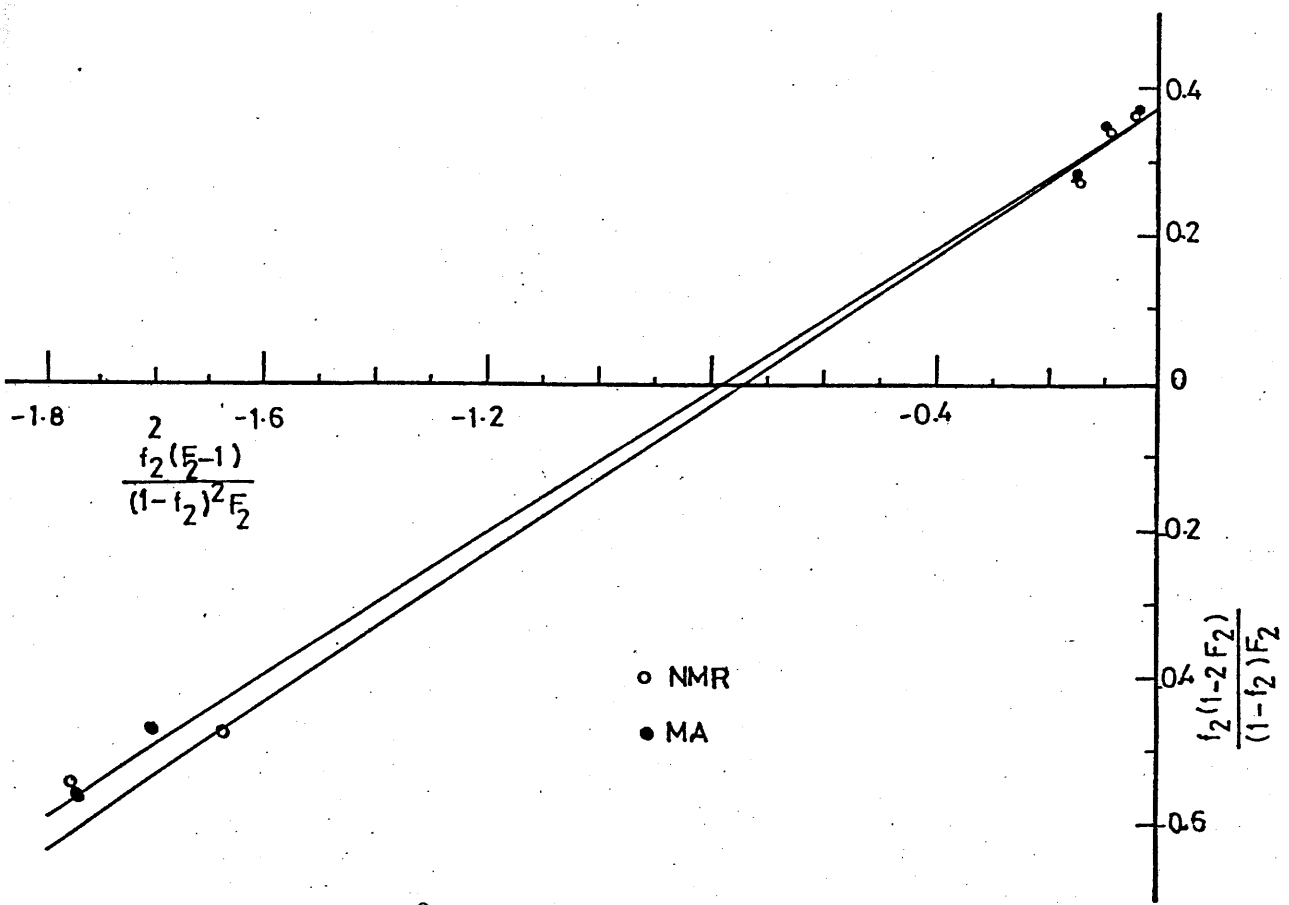


Fig.3.12. Graph of $\frac{f_2^2\ (F_2-1)}{(1-f_2)^2\ F_2}$ versus $\frac{f_2\ (1-2F_2)}{(1-f_2)\ F_2}$ for

2,3 - D B P M - Styrene copolymers.

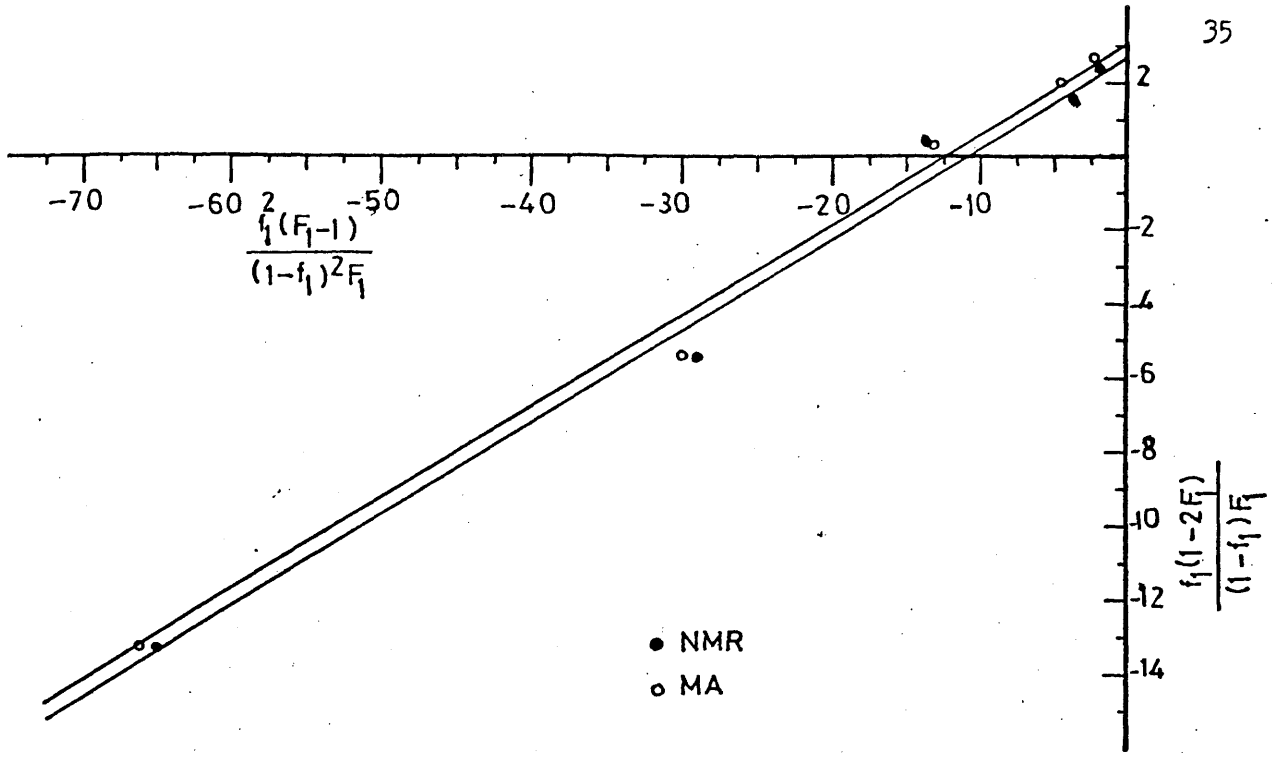


Fig. 3.13. Graph of $\frac{f_1^2 (F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1 (1-2F_1)}{(1-f_1) F_1}$ for 2,3 - D B P M - M A copolymers.

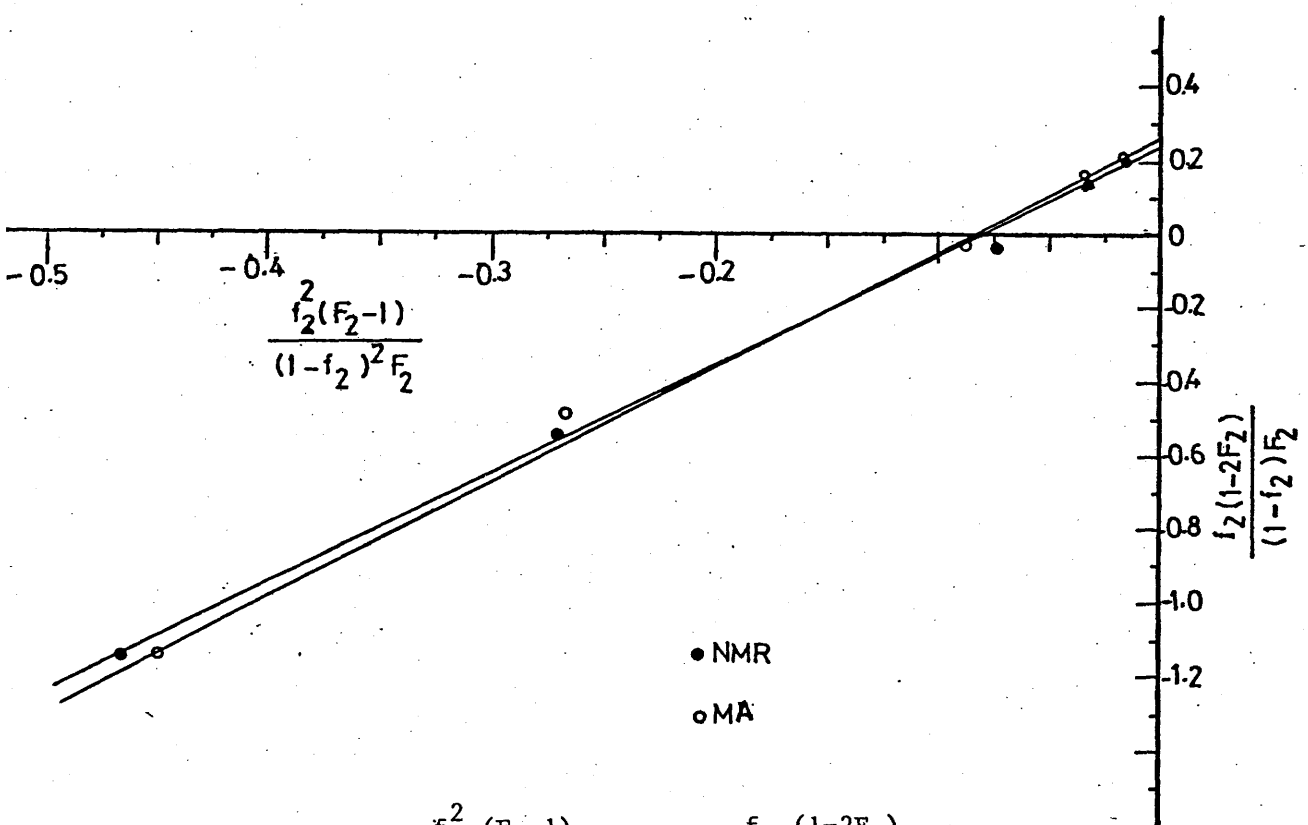


Fig. 3.14. Graph of $\frac{f_2^2 (F_2-1)}{(1-f_2)^2 F_2}$ versus $\frac{f_2 (1-2F_2)}{(1-f_2) F_2}$ for 2,3 - D B P M - M A copolymers.

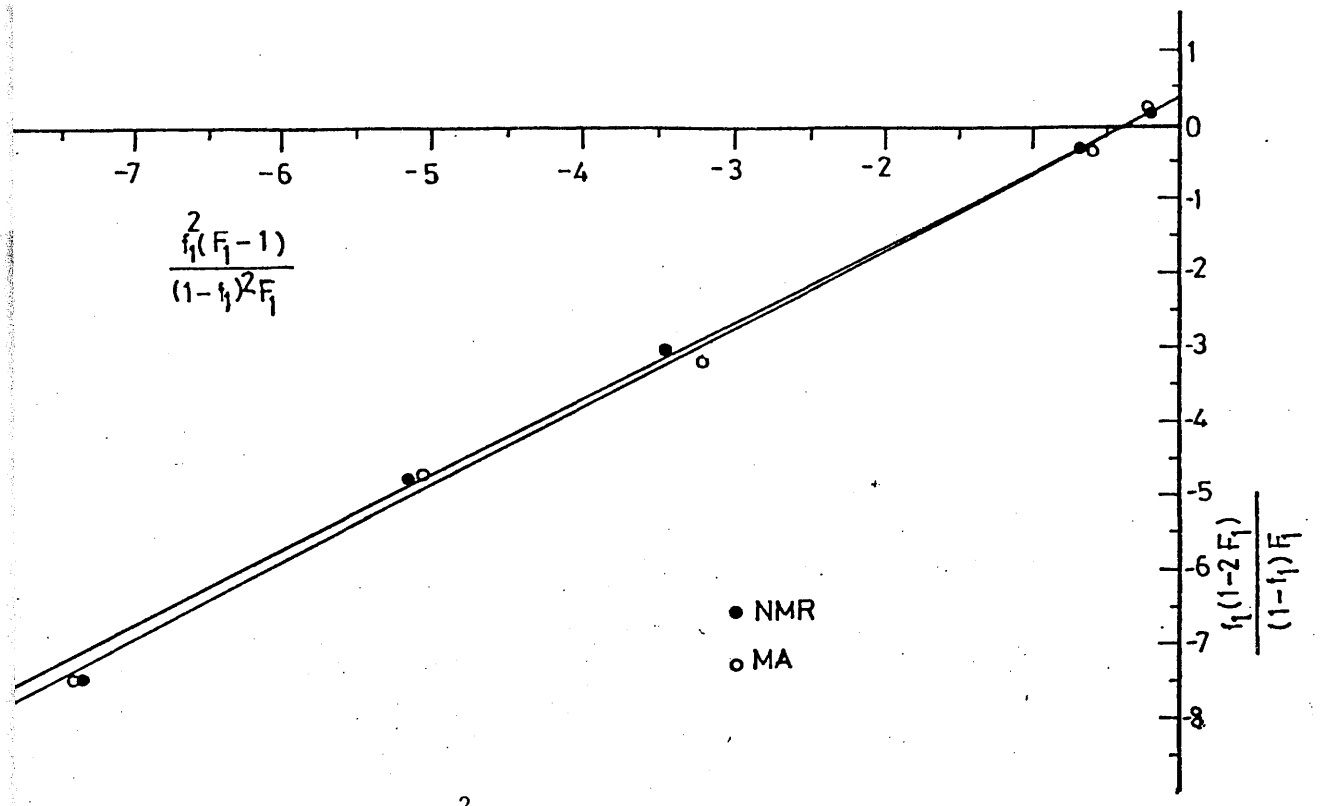


Fig. 3.15. Graph of $\frac{f_1^2\ (F_1-1)}{(1-f_1)^2\ F_1}$ versus $\frac{f_1\ (1-2F_1)}{(1-f_1)\ F_1}$ for 2,3 - D B P A - M M A copolymers.

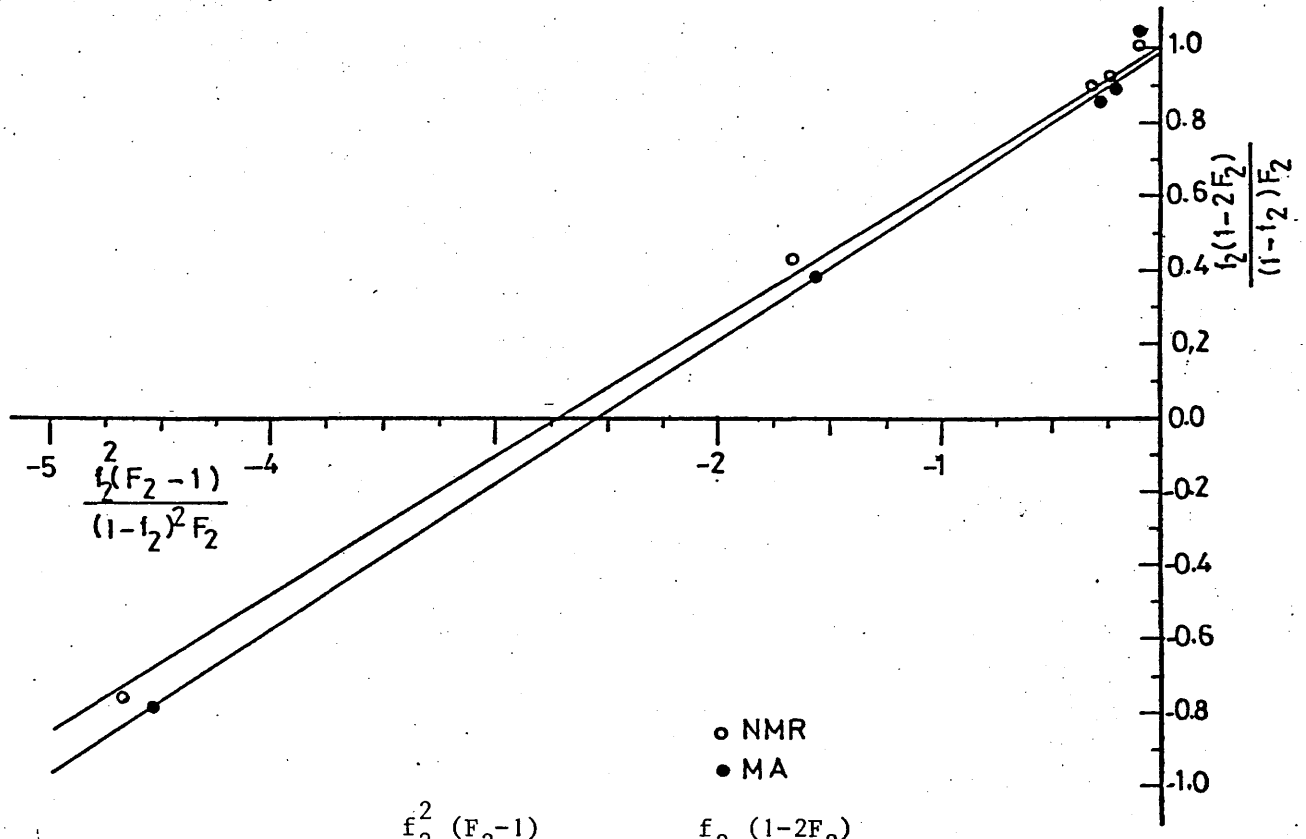


Fig. 3.16. Graph of $\frac{f_2^2\ (F_2-1)}{(1-f_2)^2\ F_2}$ versus $\frac{f_2\ (1-2F_2)}{(1-f_2)\ F_2}$ for 2,3 - D B P A - M M A copolymers.

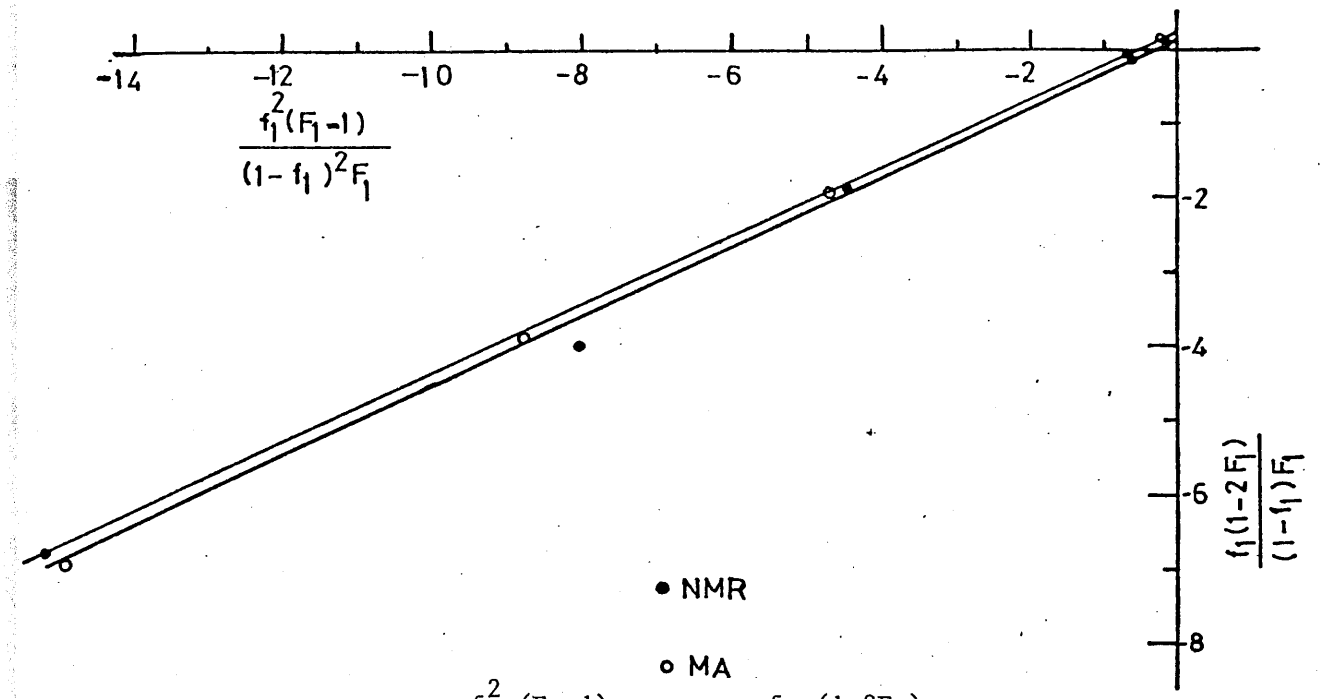


Fig.3.17. Graph of $\frac{f_1^2\ (F_1-1)}{(1-f_1)^2\ F_1}$ versus $\frac{f_1\ (1-2F_1)}{(1-f_1)\ F_1}$ for 2,3 - D B P A - Styrene copolymers.

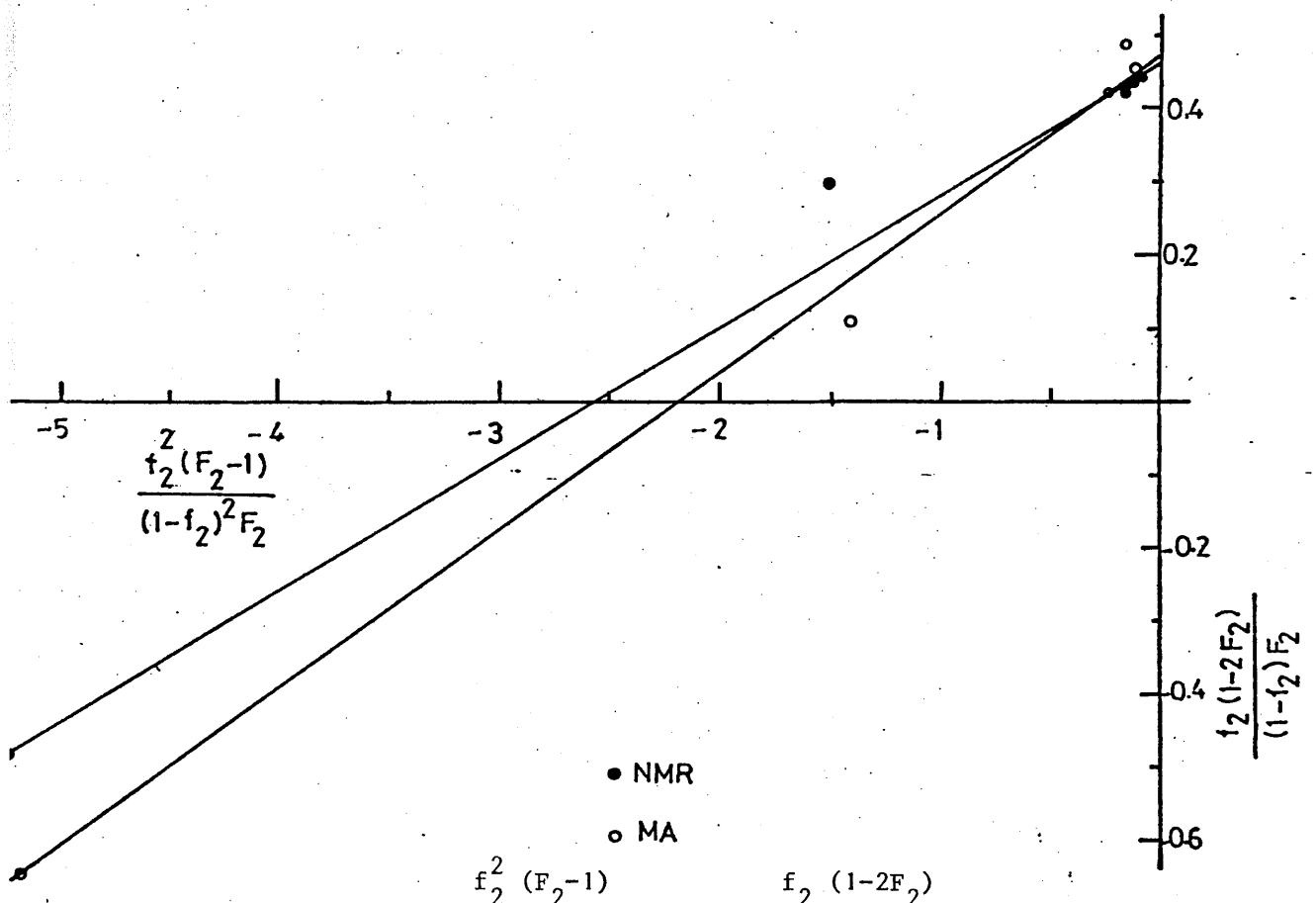


Fig.3.18. Graph of $\frac{f_2^2\ (F_2-1)}{(1-f_2)^2\ F_2}$ versus $\frac{f_2\ (1-2F_2)}{(1-f_2)\ F_2}$ for 2,3 - D B P A - Styrene copolymers.

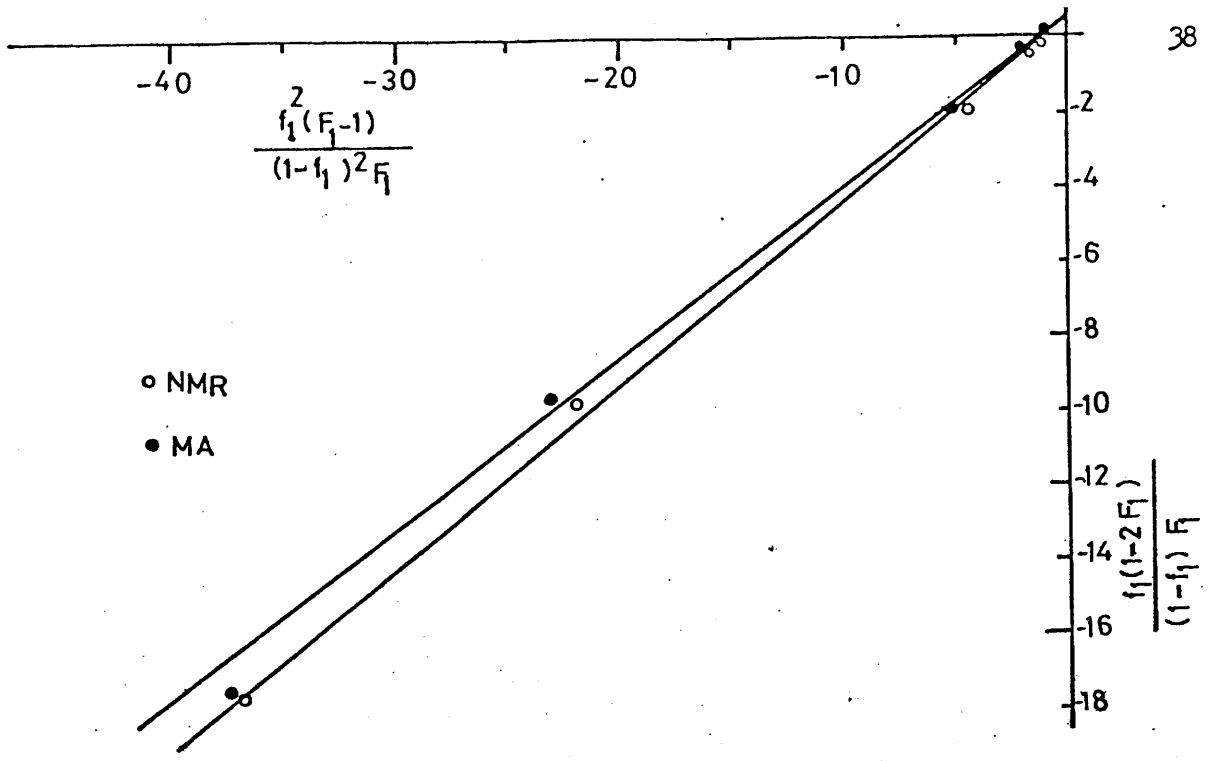


Fig. 3.19. Graph of $\frac{f_1^2 (F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1) F_1}$ for 2,3 - D B P A - M A copolymers.

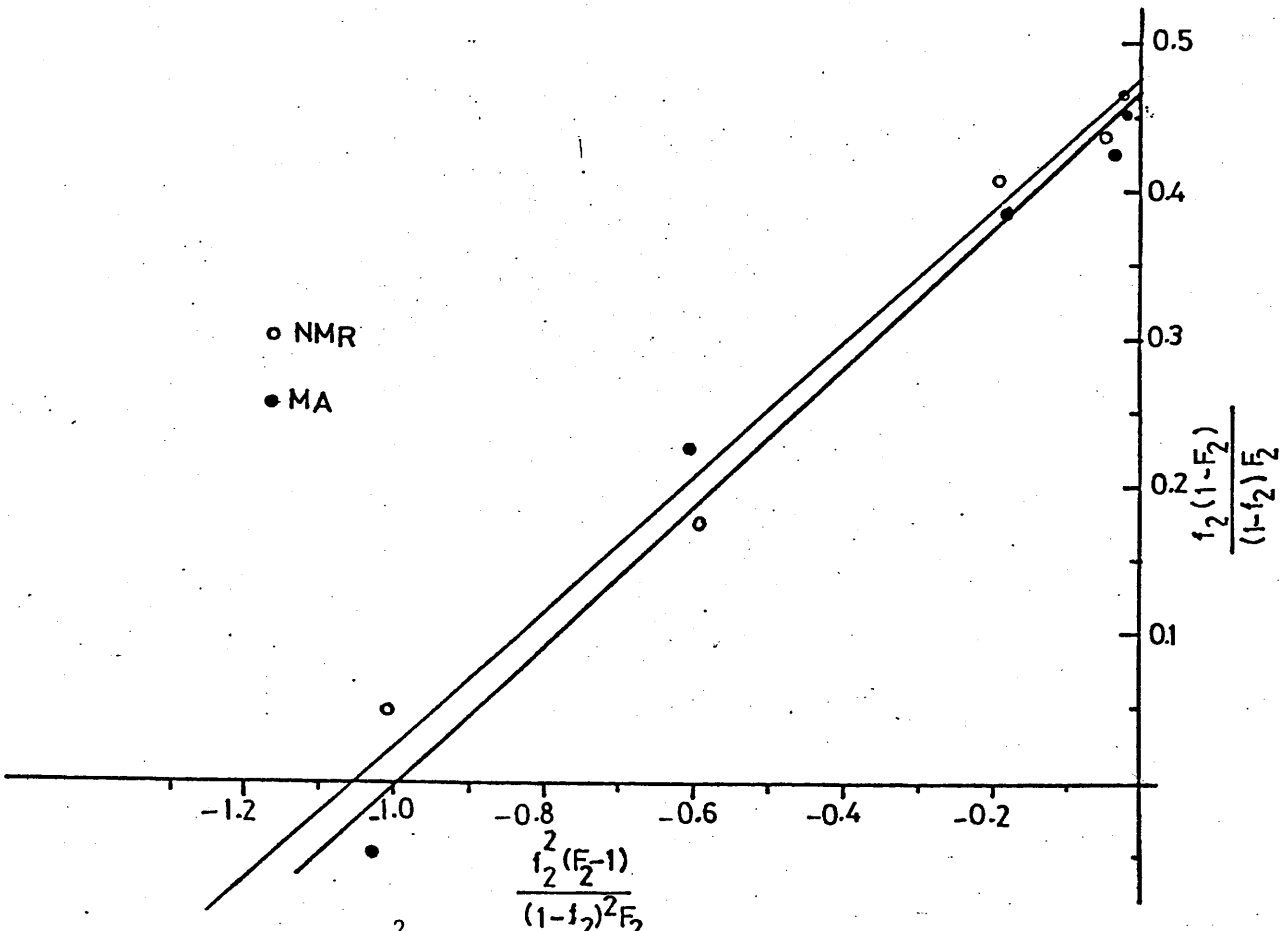


Fig.3.20. Graph of $\frac{f_2^2 (F_2-1)}{(1-f_2)^2 F_2}$ versus $\frac{f_2 (1-F_2)}{(1-f_2) F_2}$ for 2,3 - D B P A - M A copolymers.

Table 3. 3. Reactivity Ratio Values

Monomer Pair		Microanalysis		N M R	
M_1	M_2	r_1	r_2	r_1	r_2
2,3 - D B P M	M M A	0.56 ± 0.1	0.74 ± 0.1	0.65 ± 0.1	0.63 ± 0.1
	S	0.52 ± 0.1	0.37 ± 0.1	0.52 ± 0.1	0.37 ± 0.1
	M A	3.1 ± 0.2	0.24 ± 0.02	2.9 ± 0.2	0.25 ± 0.02
2,3 - D B P A	M M A	0.38 ± 0.02	1.02 ± 0.2	0.39 ± 0.02	1.03 ± 0.2
	S	0.22 ± 0.02	0.47 ± 0.1	0.17 ± 0.02	0.46 ± 0.1
	M A	0.44 ± 0.1	0.46 ± 0.1	0.43 ± 0.1	0.48 ± 0.1

CHAPTER 4

THERMAL DEGRADATION of P 2,3 - D B P M and P 2,3 - D B P A HOMOPOLYMERS

4. 1 INTRODUCTION

The thermal degradation of P 2,3 - D B P M and P 2,3 - D B P A homopolymers have not been previously reported. In this chapter the thermal degradation behaviours of these homopolymers will be discussed, their degradation products reported either qualitatively or quantitatively, and finally their degradation mechanisms discussed. The two homopolymers were prepared by the methods outlined in Chapter 2. The Number Average Molecular Weights of the P 2,3 - D B P M and P 2,3 - D B P A are 443,000 and 390,000 respectively.

4. 2 THERMAL DEGRADATION OF P 2,3 - D B P M

i. Thermal Volatilisation Analysis (T V A)

The T V A thermogram of P 2,3 - D B P M from ambient temperature to 500°C (figure 4. 1) shows a relatively sharp main peak followed by a small broad peak. Volatilisation starts at 197°C with T_{max} at 325°C and 405°C. All the traces are separated to some extent, suggesting that products with a range of volatilities are being evolved. The -196°C trace indicates that a non-condensable fraction is also being formed. A substantial cold ring fraction was coloured deep yellow and was dissolved in chloroform for infra-red spectroscopic analysis. A small amount of residue remained at 500°C accounting for only 6% of the original weight.

ii. T G, D T A and D S C

T G, D T A and D S C traces are illustrated in figure 4. 2. The

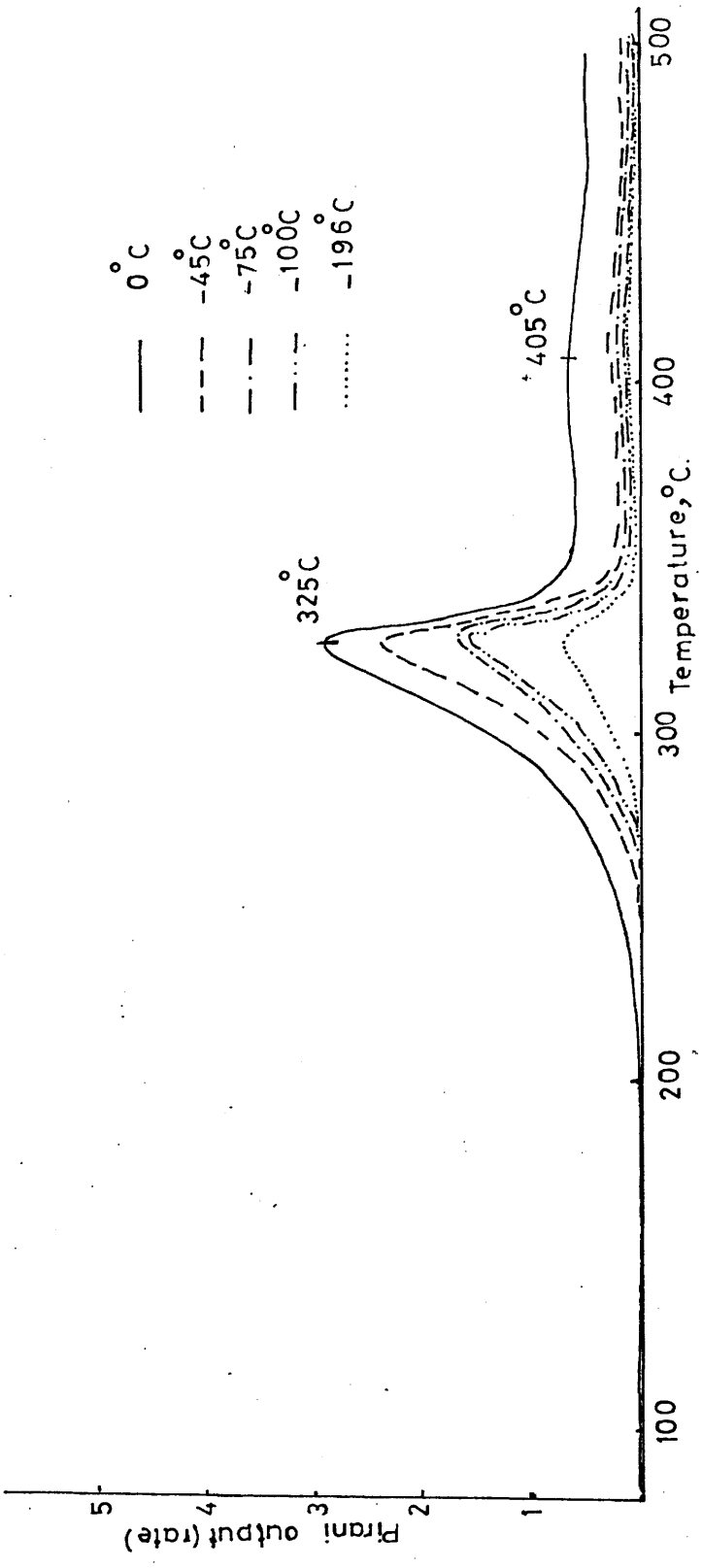


Fig. 4.1. T V A thermogram for P2,3 - D B P M. Sample size, 25 mg; heating rate 10°C/min.

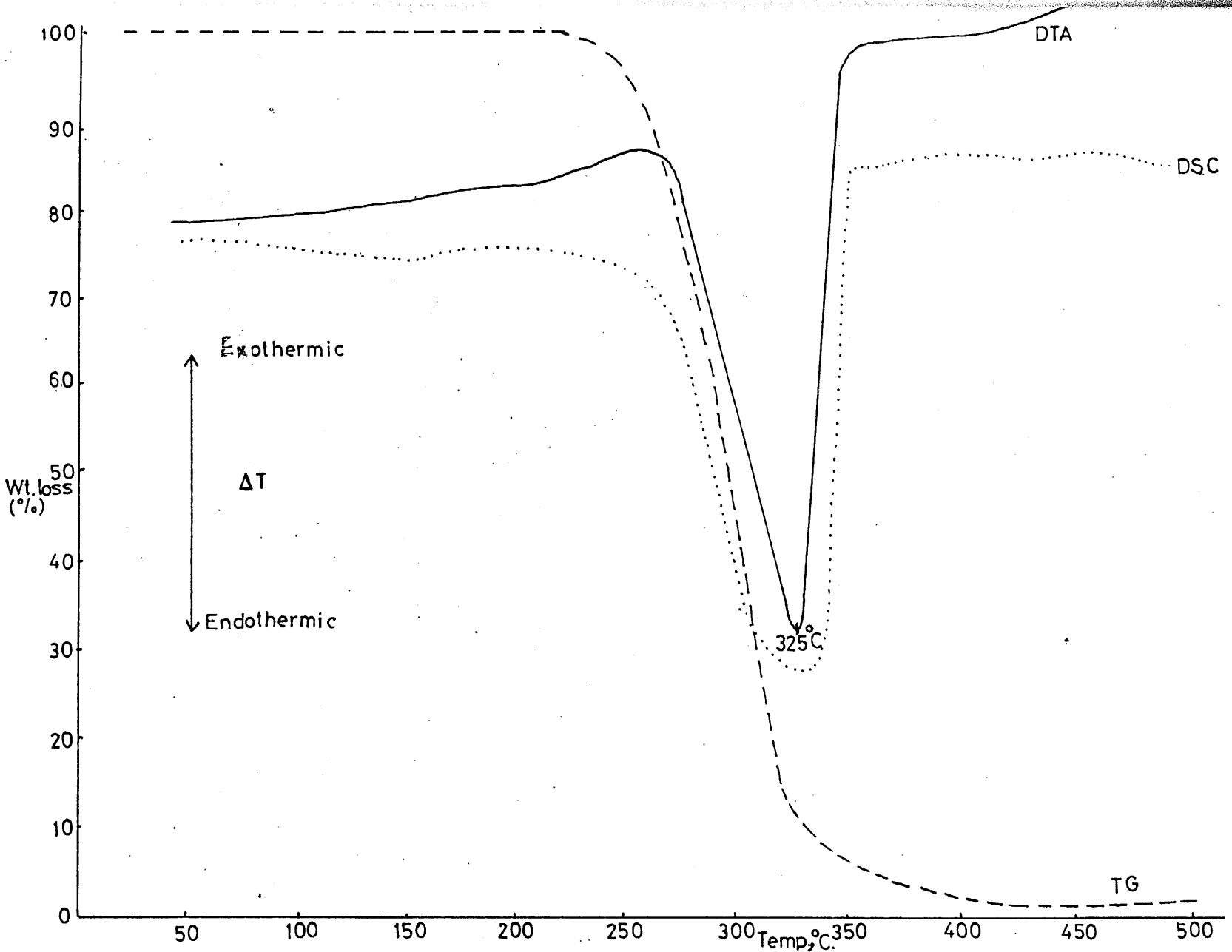


Fig. 4.2. T G , D T A and D S C curves for P2,3 - D B P M.

T G curve obtained under nitrogen has two distinct stages. In the first stage, weight loss starts at ~200°C and continues to 340°C with 85% weight loss. The maximum rate of weight loss, shown by derivative equipment associated with the T G apparatus, occurs at 325°C. The second stage reaches a maximum at ~400°C. Both D T A and D S C curves gave endothermic peaks at 325°C.

iii. Product Analysis and Subambient T V A

The degradation products of P 2,3-D B P M consist of a number of fractions.

a. The non-condensable materials were collected in a closed system after degradation of separate samples at various temperatures (300°, 400° and 500°C) for one hour. Infra-red spectra showed that carbon monoxide, methane and propene are formed at all these temperatures and this was confirmed by mass spectral measurements (figure 4.3).

b. The infra-red spectrum of the cold ring fraction (figure 4.4) shows the formation of anhydride which is indicated by the shoulders at 1795 and 1750 cm^{-1} on the carbonyl peak.

c. The black residue which remains on the base of the degradation tube has no well defined i r spectral features and is assumed to be principally carbon.

d. The condensable products were subjected to subambient T V A as described in Chapter 2, with the result shown in figure 4.5. I r and mass spectra for the material in peaks 1 and 2 combined are shown in figure 4.6 and 4.7(a). Mass spectra and g l c data for the material in peaks 3 and 4 are shown in figures 4.8(a), 4.8(b), and 4.9. The mass spectra of some reference materials are shown in figures 4.7(b) and 4.8(c, d and e). Thus, the degradation products

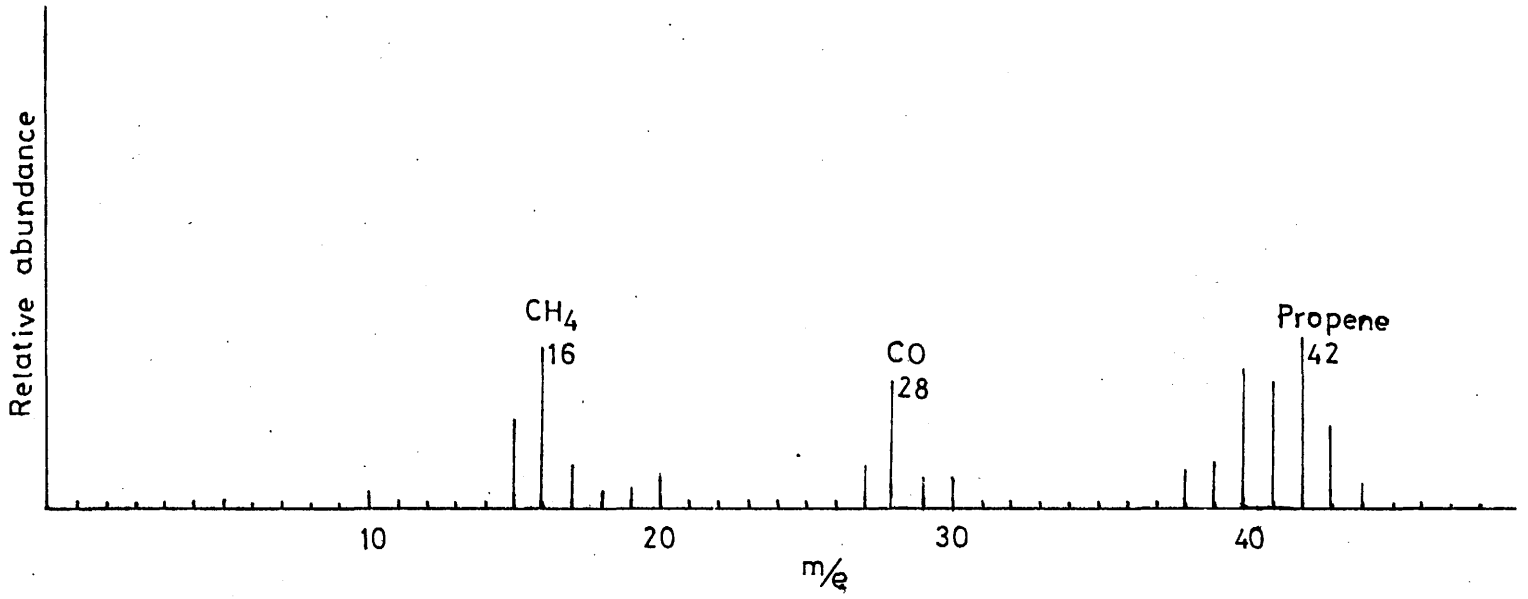


Fig. 4.3. Mass spectra of non-condensable materials from the degradation of P2,3 - D B P M isothermally at 300°C for 1 hour.

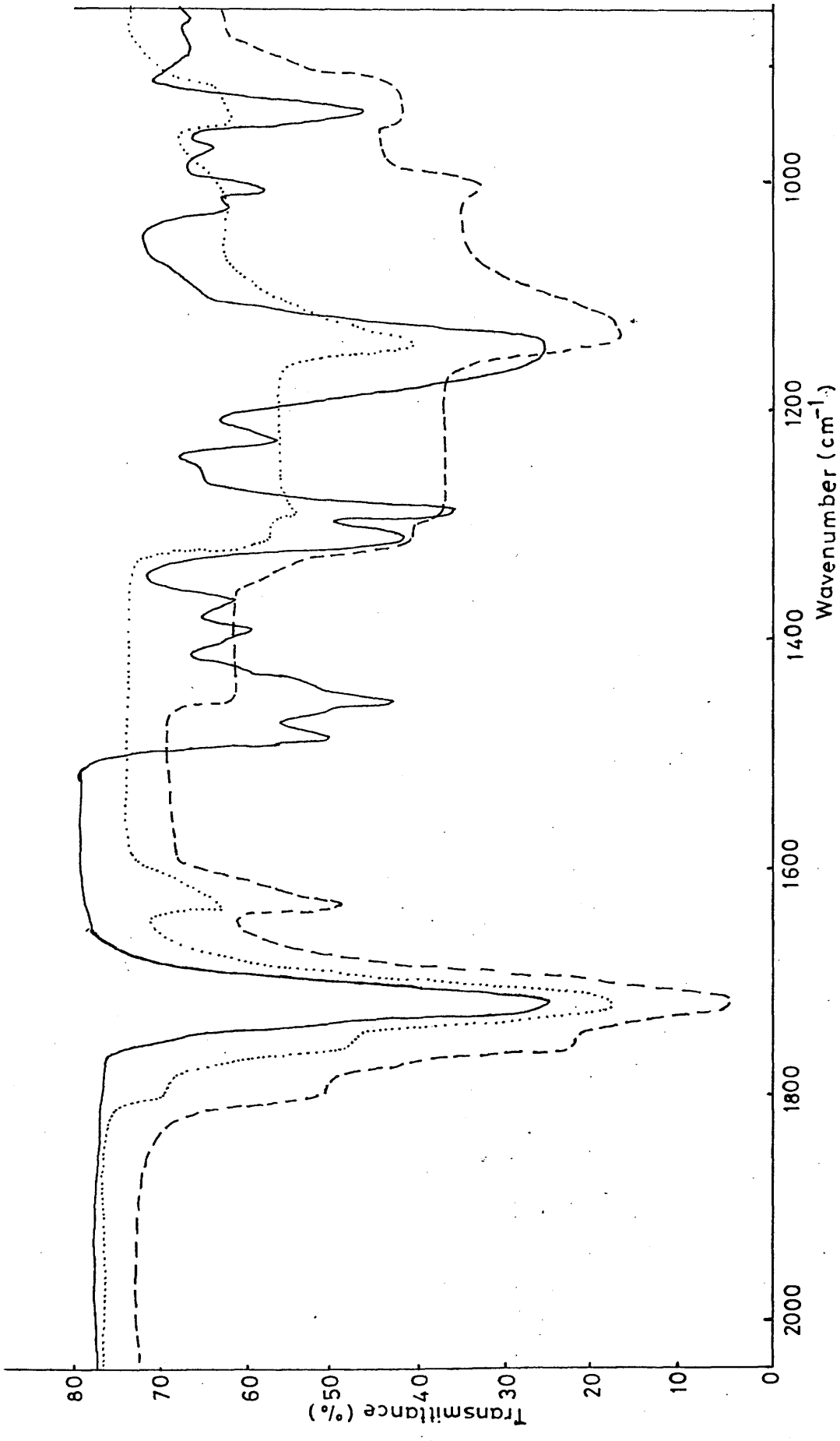


Fig. 4.4. The 900 - 2000 cm^{-1} region of the infra-red spectra of (—), undegraded P2,3 - D B P M (····), C R F at 400°C and (– –), at 500°C.

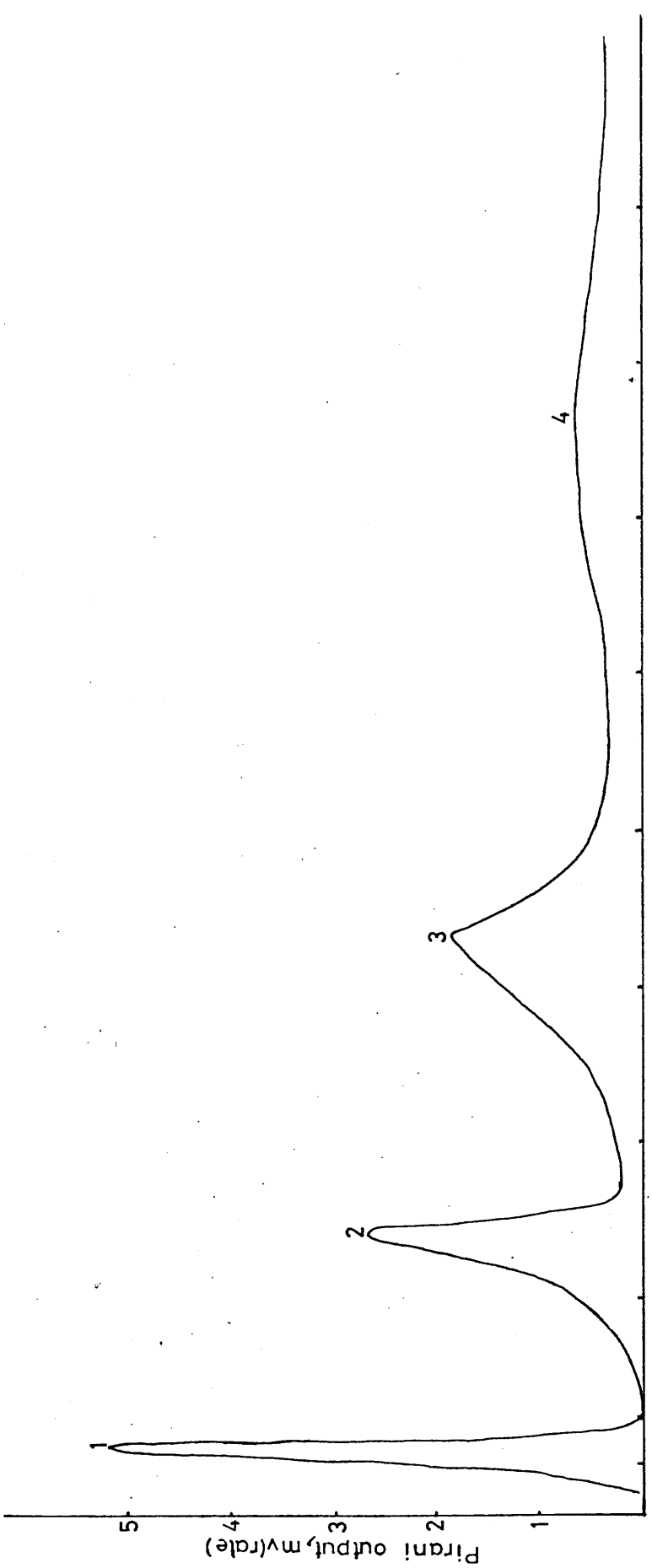


Fig.4.5. Subambient T V A curve for degradation products of P2,3 - D B P M (from Programmed degradation under vacuum to 500°C at 10°C/min. ; 50 mg sample).

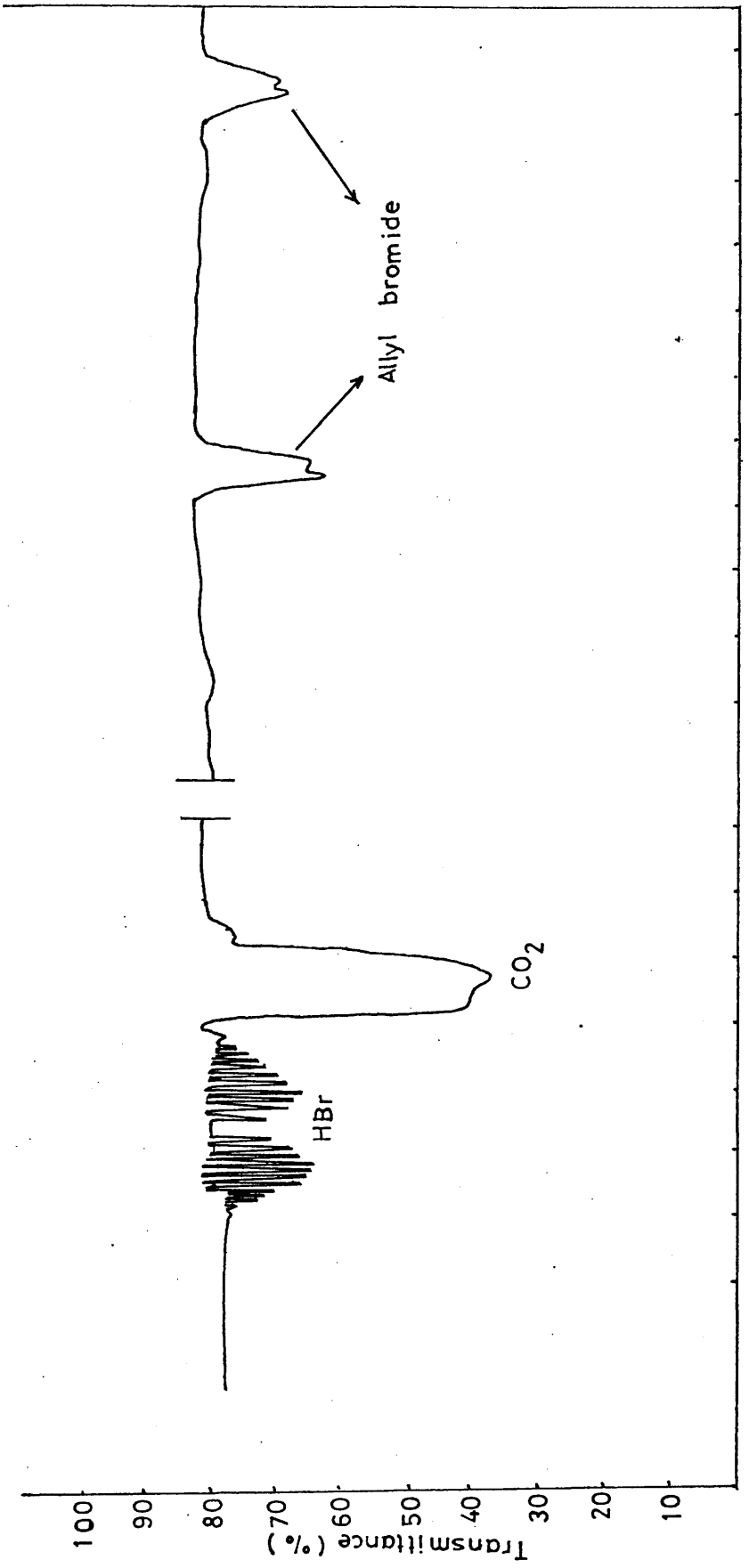


Fig. 4.6. The 900 - 3000 cm^{-1} region of the infra-red spectra of peaks 1 and 2 in the subambient T V A curve (figure 4.5).

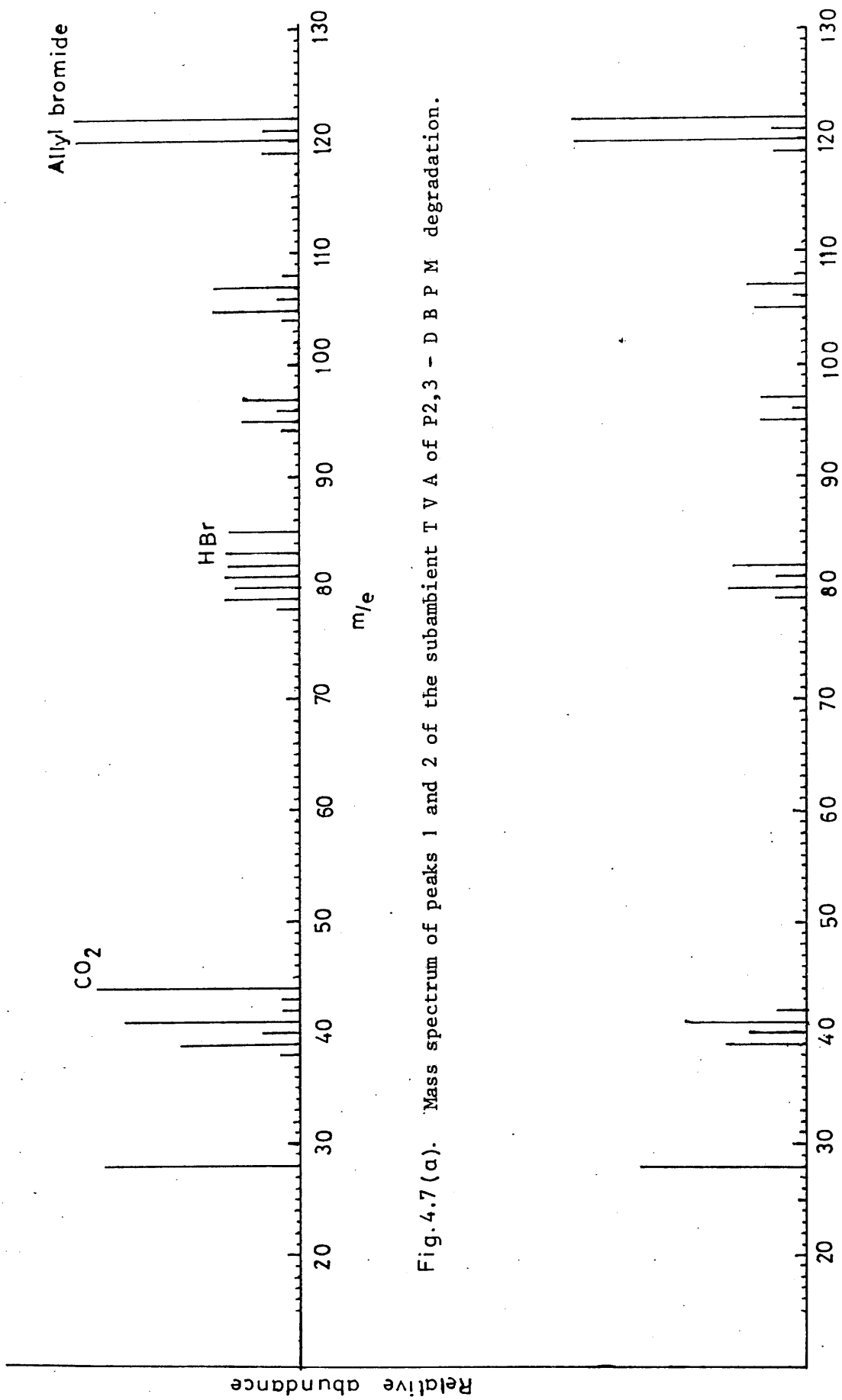


Fig.4.7(a). Mass spectrum of peaks 1 and 2 of the subambient T V A of P2,3 - D B P M degradation.

Fig.4.7(b). Mass spectrum of allyl bromide (reference).

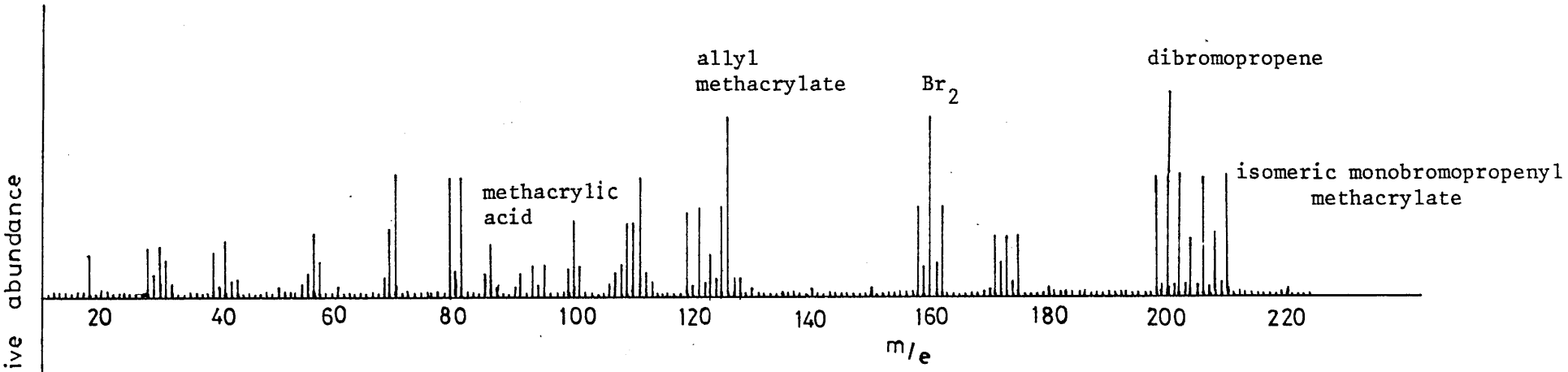


Fig .4.8 (a) Mass spectrum of peak 3 of the subambient T V A of P2,3 - D B P M degradation.

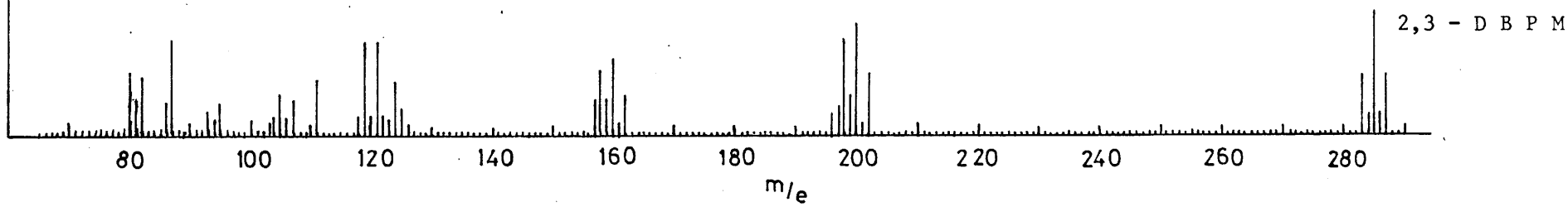


Fig.4.8 (b) Mass spectrum of peak 4 of the subambient T V A of P2,3 - D B P M degradation.

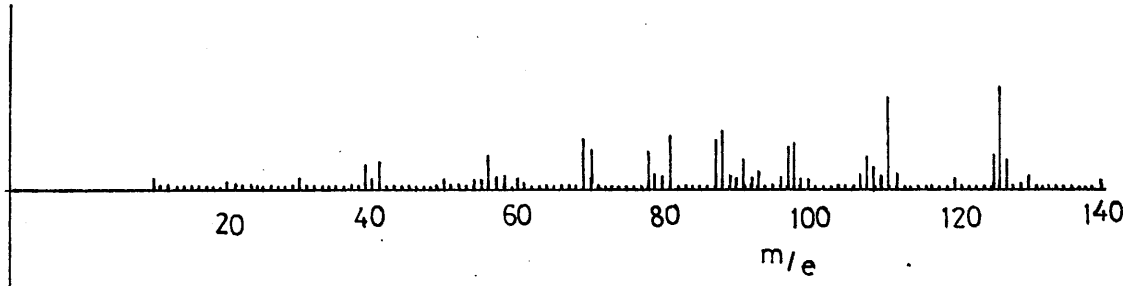


Fig.4.8 (c). Mass spectrum of allyl methacrylate (reference).

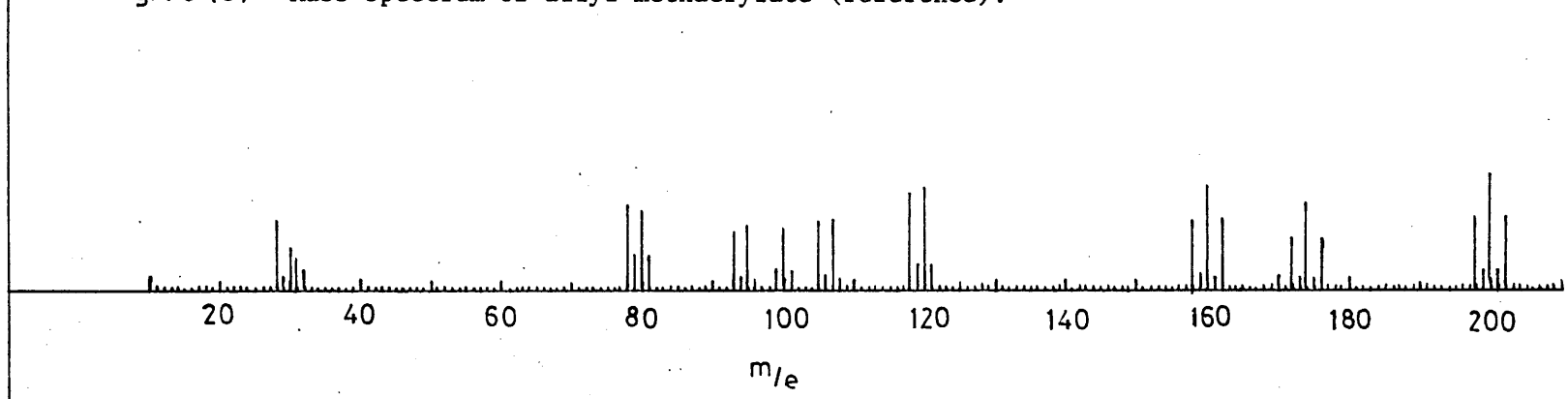


Fig.4.8 (d) Mass spectrum of 2,3 - dibromoprop-1-ene (reference).

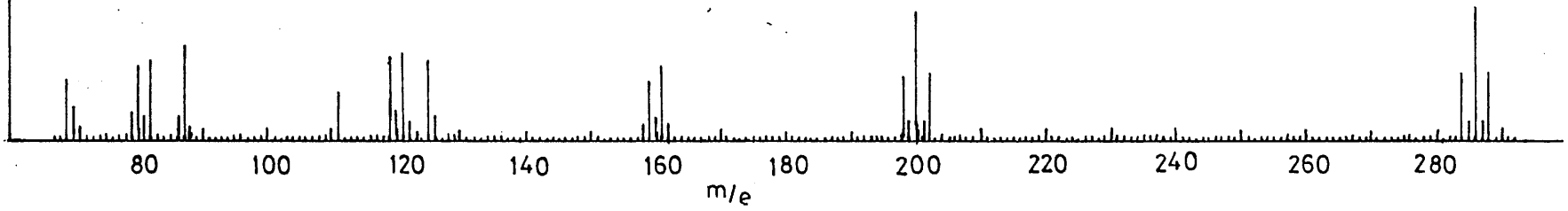


Fig.4.8(e) Mass spectrum of 2,3 - D B P M (reference).

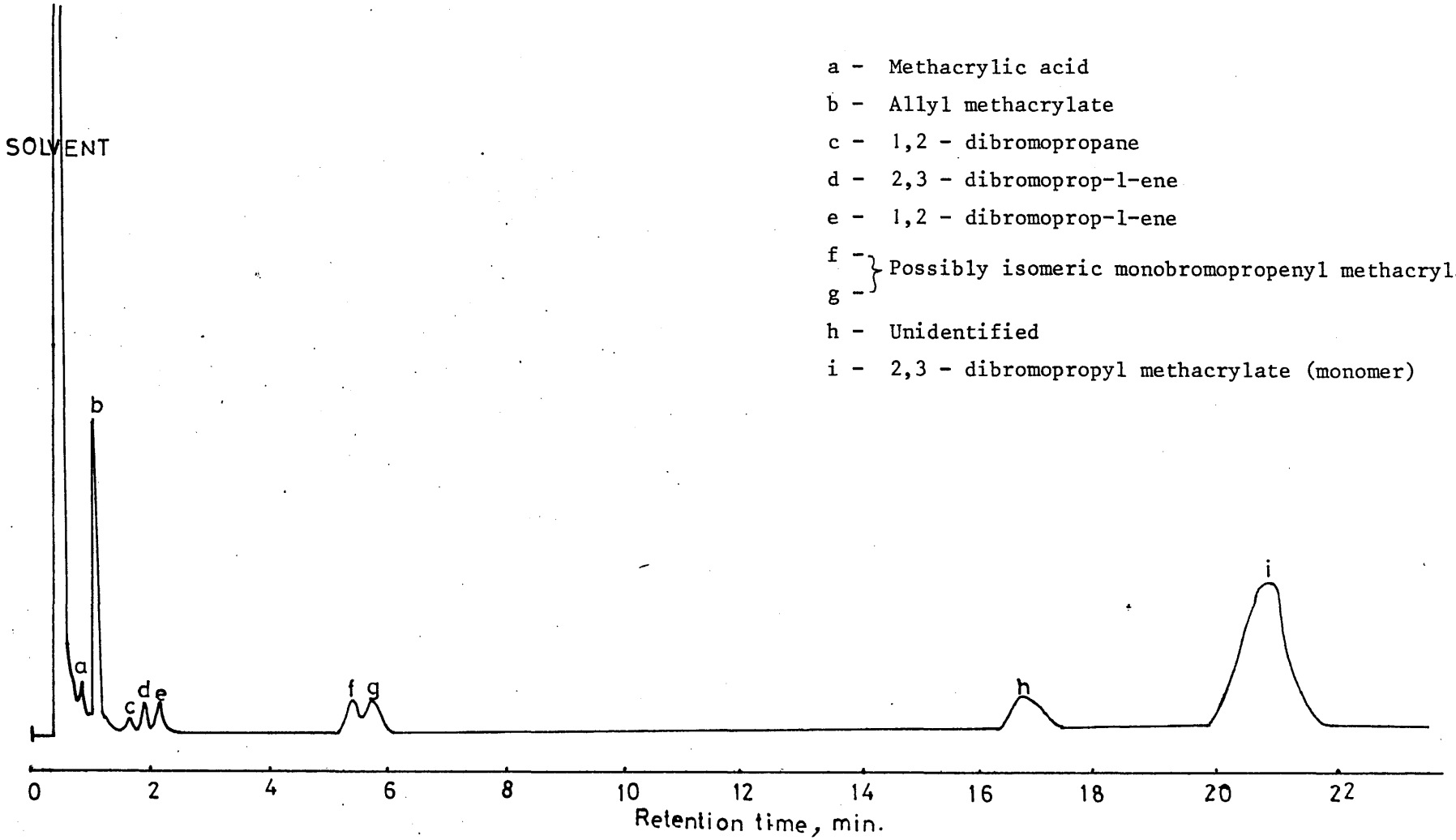
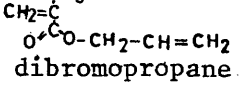


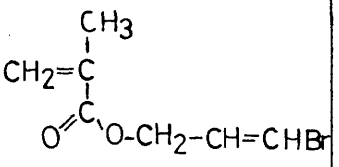
Fig.4.9. G l c trace for the degradation products of peaks 3 and 4 in the subambient T V A curve (figure 4. 5) by using 5 ft. ¼ inch diameter : 10% microwax on chromosorb column isothermally at 140°C.

of P 2,3-D B P M have been identified as in Table 4.1, although the unavailability of some reference compounds means that the identities of some of the minor products have been assigned only tentatively from the mass spectral data. These products are indicated by *.

TABLE 4.1. DEGRADATION PRODUCTS OF P 2,3-D B P M

Degradation fraction	Products	Methods of analysis
Non-condensable materials	CH_4 , CO , propene	I R & M S
C R F	Poly (methacrylic anhydride)	I R in solution
Residue	Carbon	I R (KBr disc)
Condensable materials :		
Peak 1 (S A T V A)	CO_2 , HBr	I R & M S
Peak 2 (S A T V A)	Allyl bromide $CH_2 = CH-CH_2Br$	I R & M S
Peak 3 (S A T V A)	H_2O , Br_2	I R & g l c
	Methacrylic acid	M S & g l c
	Allyl methacrylate 	M S & g l c
	1,2 - dibromopropane CH_2 Br - CH Br - CH_3	M S & g l c
	Isomeric dibromopropenes	M S & g l c

Cont'd TABLE 4.1.

Degradation fraction	Products	Methods of analysis
	Isomeric monobromopropenyl methacrylates *	M S
	e.g 	
Peak 4 (S A T V A)	2,3 dibromopropyl methacrylate (monomer)	M S & g l c

The temperature ranges over which the various degradation products were evolved were identified as follows :- A sample of P 2,3-D B P M was heated in the subambient T V A apparatus from ambient temperautre to 210°C under vacuum and under programmed conditions of 10°C/min. The sample was held at this temperature and the volatile fraction was subjected to S A T V A. The sample was then programmed up to 220°C, and the process repeated. Successive temperature increases gave the series of S A T V A curves shown in figure 4.10. It is seen that peak 1 first appeared at a much higher temperature than the other three peaks. Up to 320°C, peak 1 consists of HBr only, after which CO_2 is formed continuously to 500°C. No HBr was formed above 400°C.

iv. Quantitative Measurement of Degradation Products

Infra-red spectroscopy and g l c were used for quantitative analysis of the degradation products as described in Chapter 2. I r was used

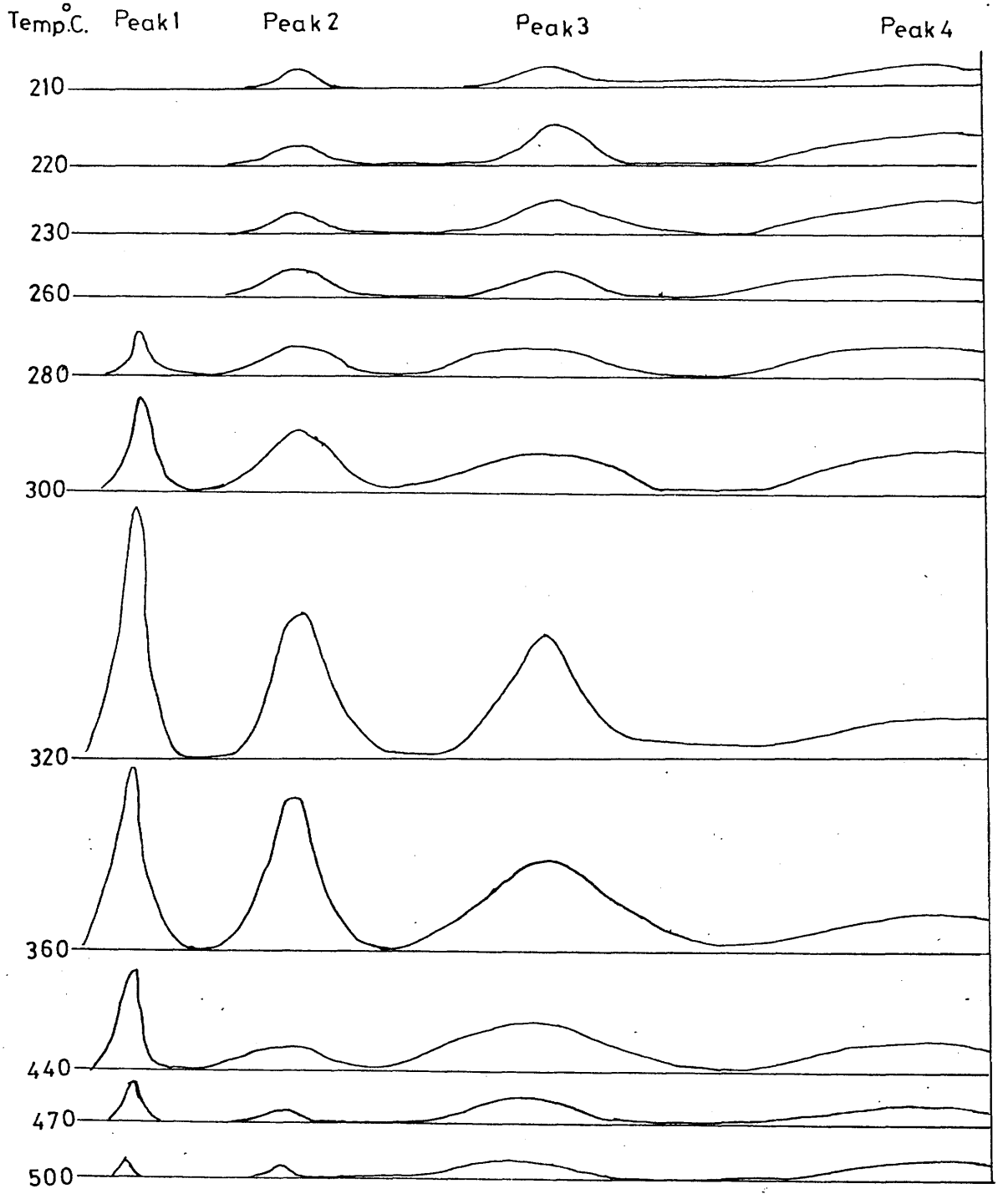


Fig.4.10. Subambient T V A curves for degradation products of a single sample of P2,3 - D B P M (for programmed degradation under vacuum from ambient to successively higher temperatures at 10°C/min , 50 mg sample size). Sample held at each temperature while products were collected for S A T V A.

for peaks 1 and 2 in the S A T V A and g l c for peaks 3 and 4. In the latter case, some minor products were unavailable for calibration purposes, and estimated retention times and sensitivities were used based on boiling points and data for structurally similar compounds. These products are indicated by * in Table 4.2, which gives the results for programmed degradation from ambient temperature to 500°C. Values marked * should be regarded as only qualitative.

Table 4.2. QUANTITATIVE ANALYSIS OF THE PRODUCTS OF DEGRADATION OF P 2,3 -D B P M (20°- 500°C at 10°/min)

Product	wt.% of original polymer
HBr	12.2
CO_2	2.6
Propene	0.2
Allyl bromide	2.5
H_2O	trace
Br_2	3.1
Methacrylic acid	trace
Allyl methacrylate	2.1
1,2 - dibromopropane	0.2
Isomeric dibromopropenes	0.6
Isomeric monobromopropenyl methacrylate *	1.8 *
2,3 - dibromopropylmethacrylate (monomer)	55.8
C R F (Poly (methacrylic anhydride))	6.0
Residue	6.0
Total products identified	93.1

4.3 THERMAL DEGRADATION OF P 2,3 -D B P A

i. Thermal Volatilisation Analysis (T V A)

Figure 4.11 shows a T V A trace for P 2,3 -D B P A. There is a sharp main peak followed by a low broad peak. Volatilisation starts at 233°C with T_{max} occurring at 331°C and 438°C. The separation of the curves shows that there are products of a wide range of volatilities and a considerable amount of material is non-condensable at -196°C. A yellow cold ring fraction is formed and may be dissolved in chloroform for i r analysis. A small amount (~3%) of residue remains at 500°C.

ii. T G and D S C

Figure 4.12 shows T G and D S C traces for P 2,3- D B P A. The T G curve, detained under nitrogen (50 ml/min) has two distinct stages. In the first stage weight loss starts at ~220°C, shows a maximum at 335°C and is complete by 350°C with 80% weight loss. The second stage (7%) reaches a maximum at ~ 430°C.

D S C shows an endothermic peak at ~335°C which is concurrent with volatilisation.

iii. Product Analysis and Subambient T V A

The degradation products of P 2,3-D B P A may be separated into fractions : a. The non-condensable materials may be collected in a closed system and their i r spectrum reveals carbon monoxide, methane and propene. Hydrogen is indicated by the mass spectrum.

b. Infra-red spectroscopy indicates that the cold ring fraction (figure 4.13) has some structural similarity to the original polymer.

c. The residue on the base of the degradation tube is a black carbonaceous char with no well developed absorptance in the i r.

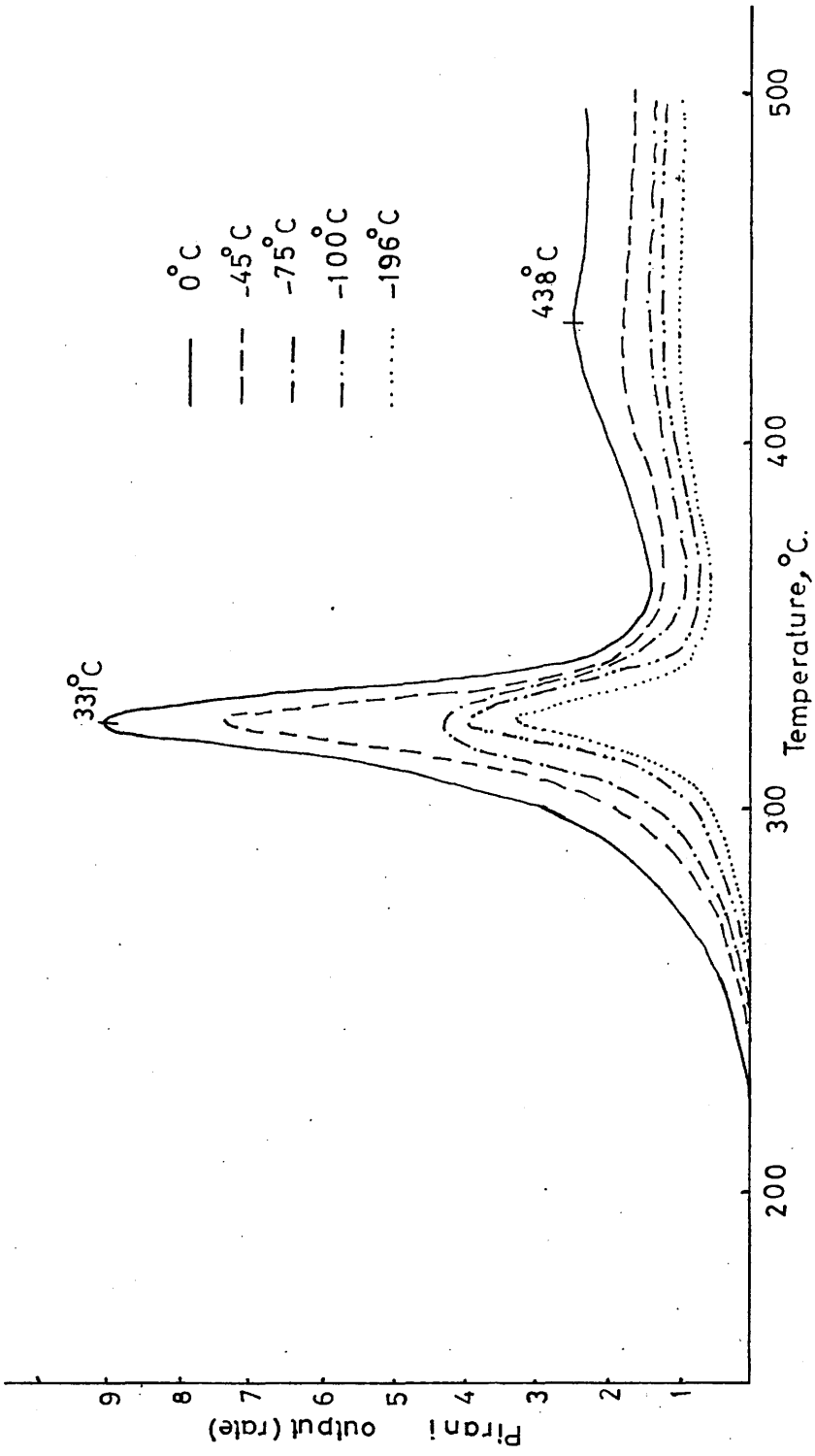


Fig.4.11. T V A thermogram for P2,3 - D B P A. Sample size 25 mg , small pieces; heating rate 10^{o}C/min.

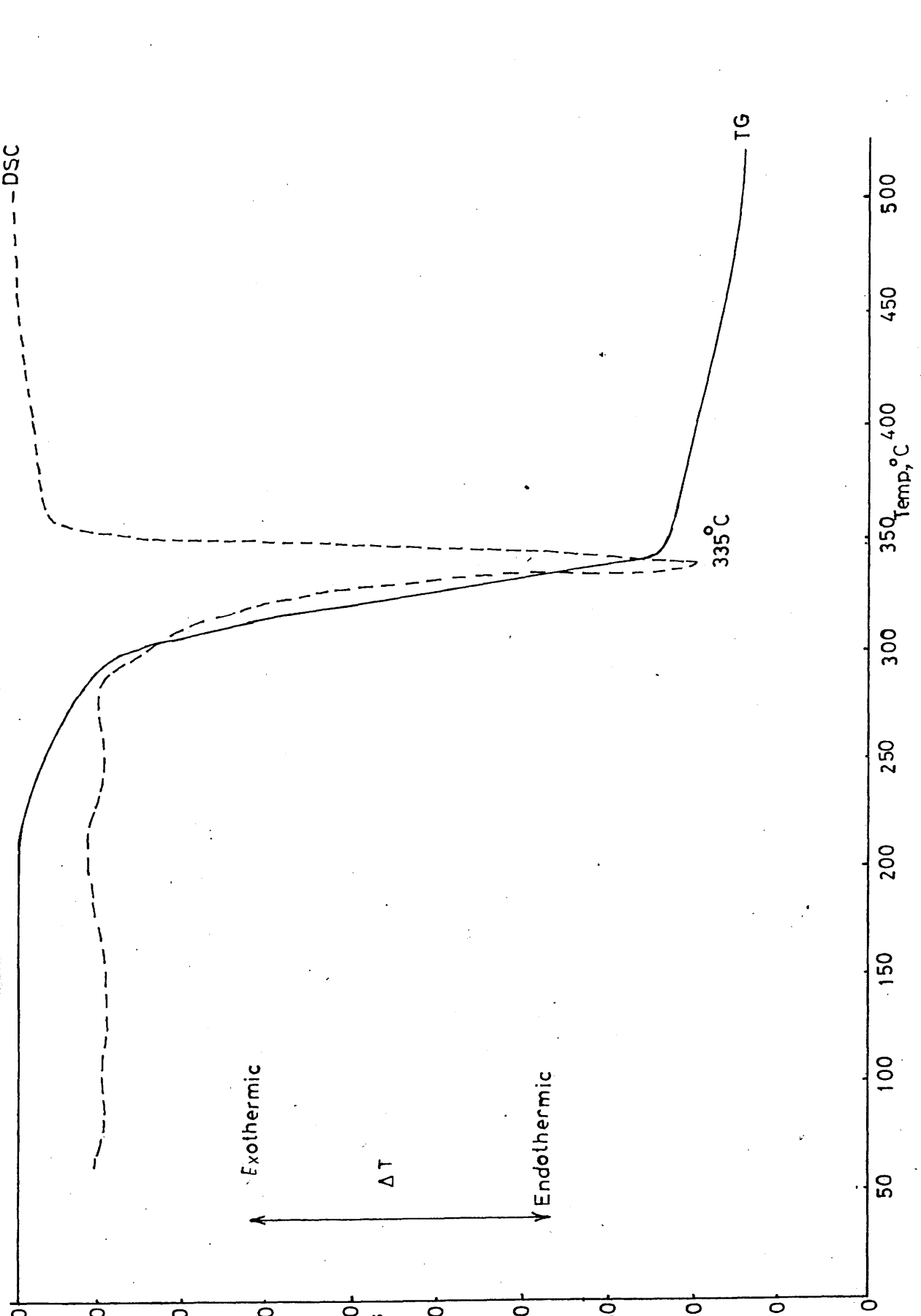


Fig. 4.12. T G and D S C curves for P2,3 - D B P A.

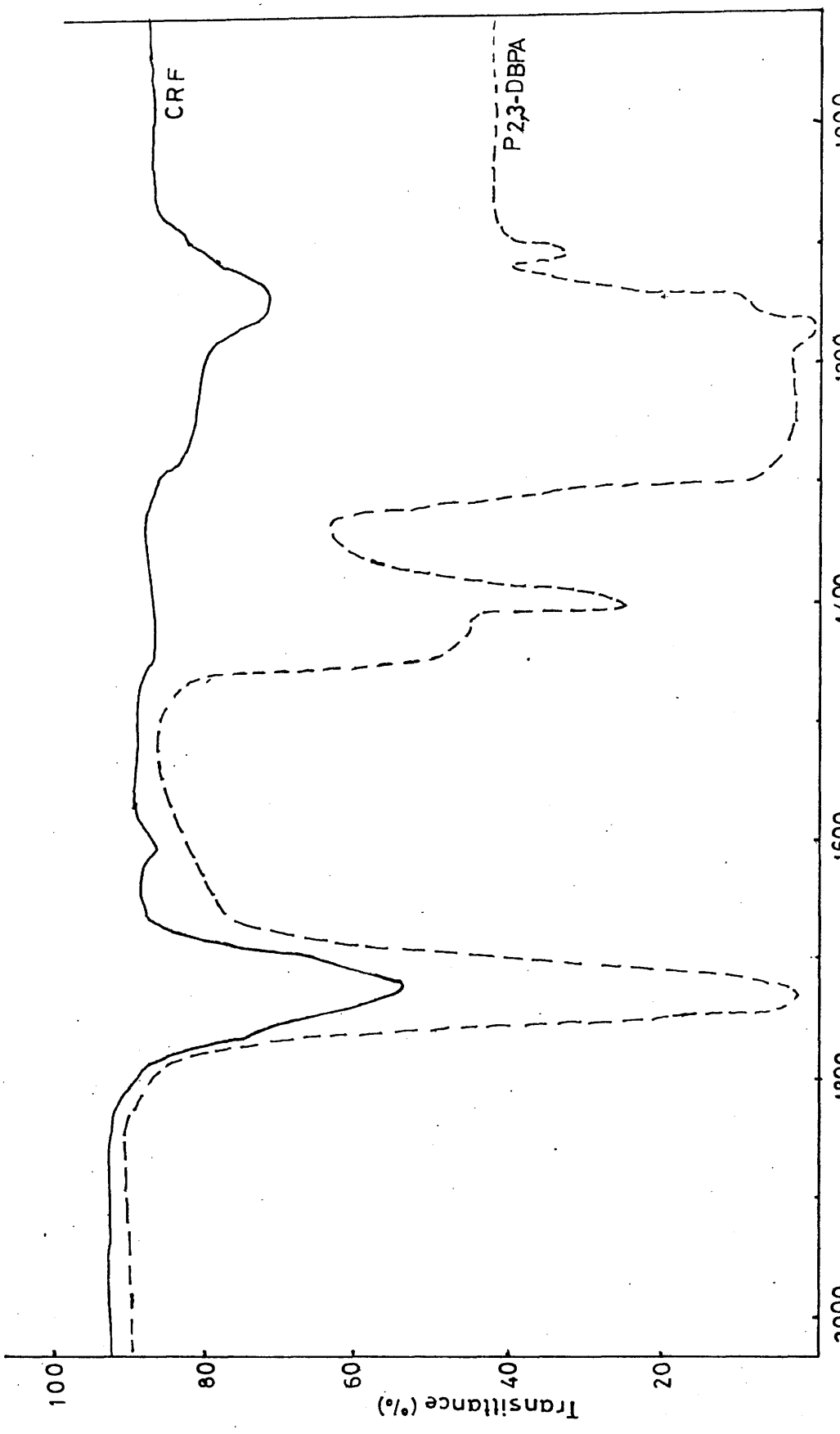


Fig.4.13. The 1000 - 2000 cm^{-1} region of the infra-red spectra of (---)undegraded and (—) C R F of P2,3 - D B P A.

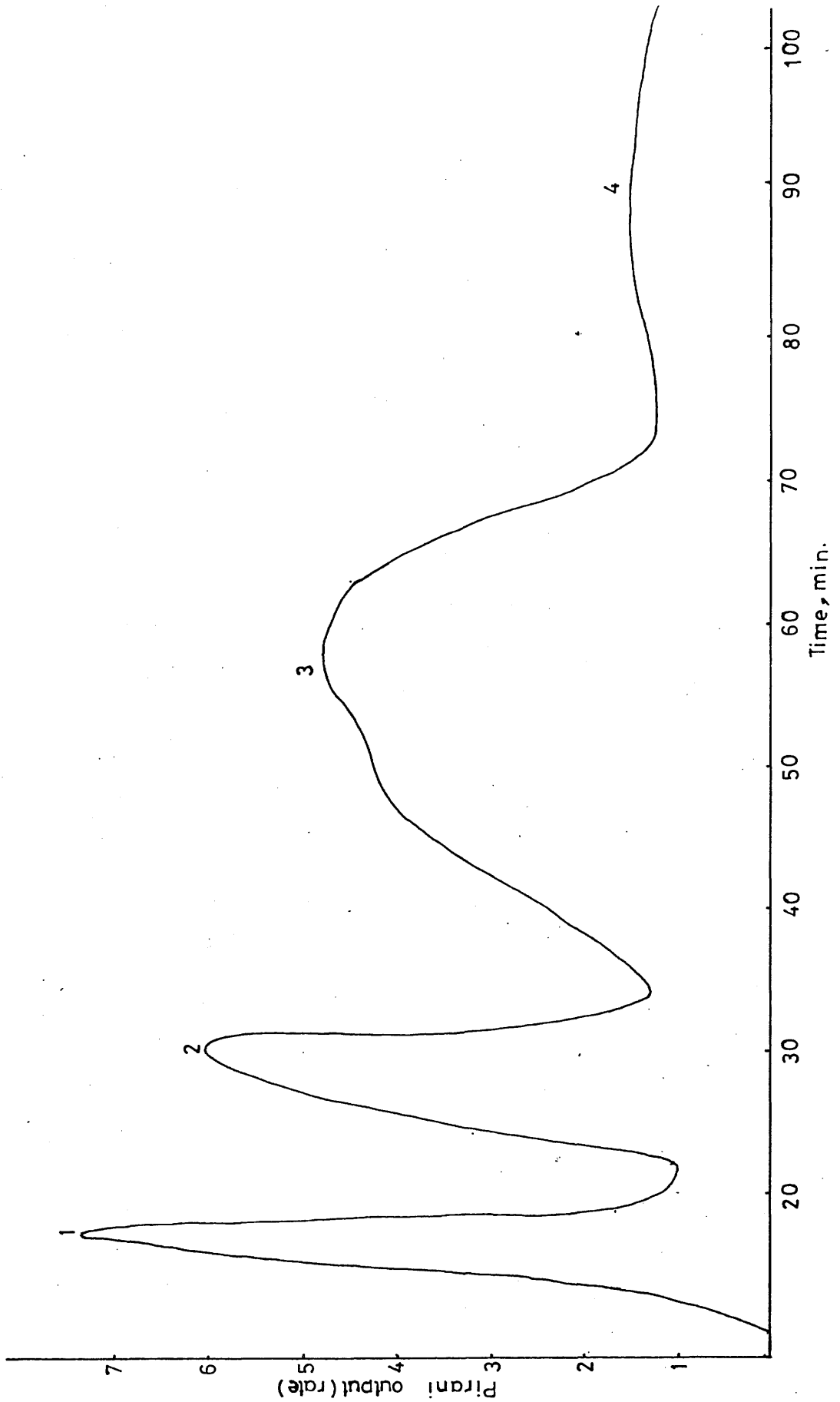


Fig. 4.14. Subambient T V A curve for degradation products of P2,3 - D B P A (from programmed degradation under vacuum to 500°C at 10°C/min , 50 mg small pieces sample size).

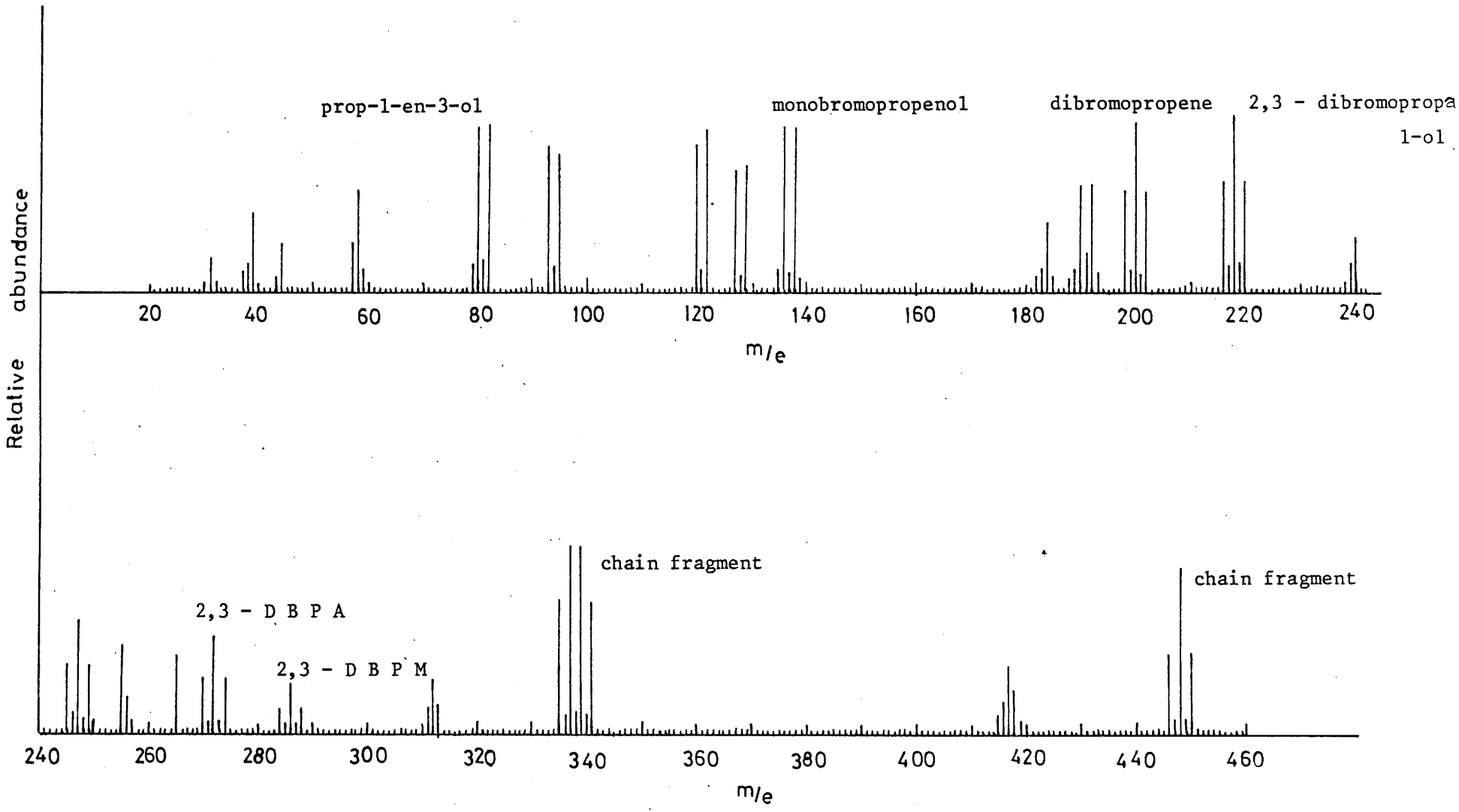
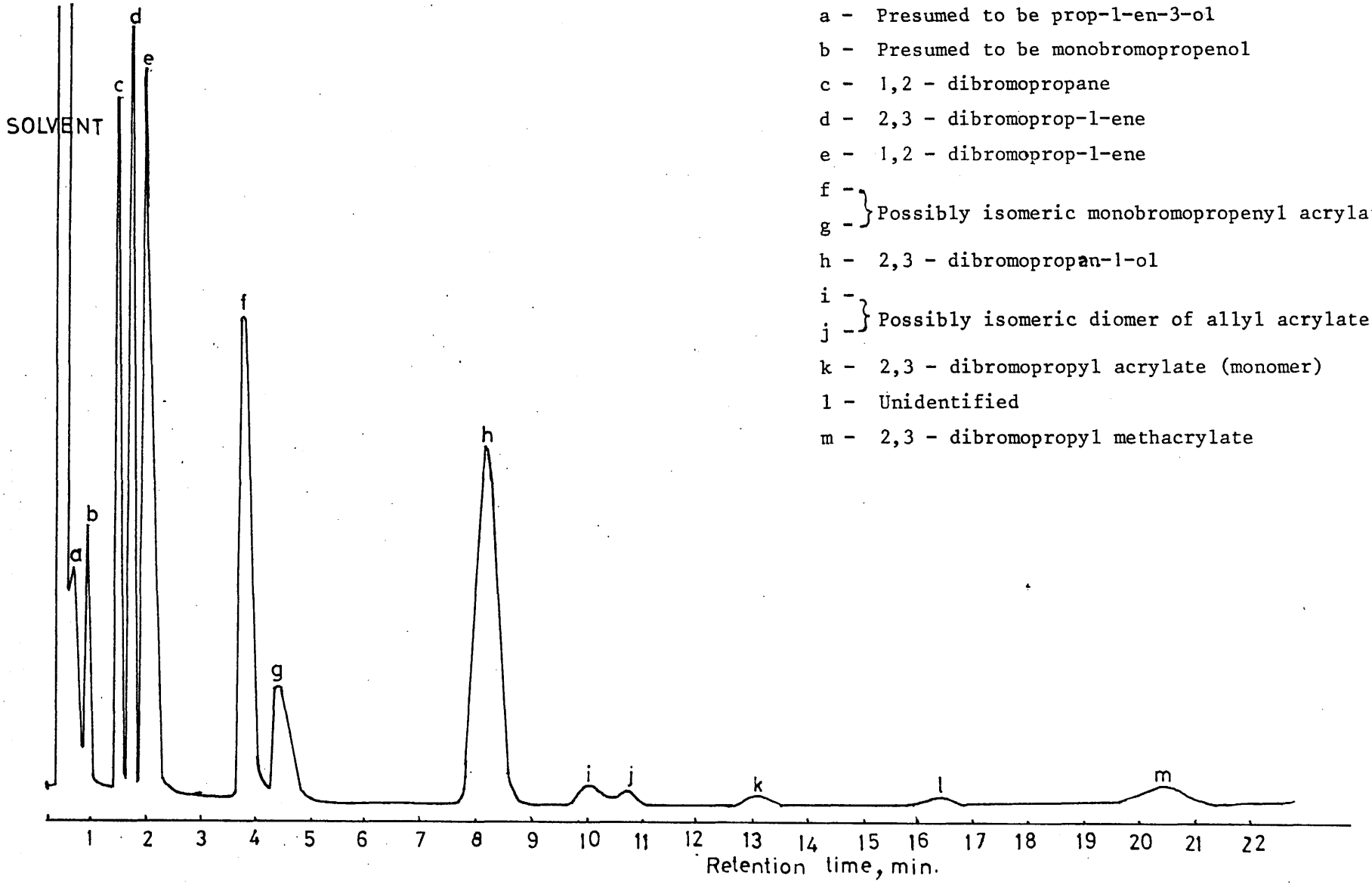


Fig. 4.15. Mass spectrum for peaks 3 and 4 in the subambient T V A of P2,3 - D B P A.



a - Presumed to be prop-1-en-3-ol
b - Presumed to be monobromopropenol
c - 1,2 - dibromopropane
d - 2,3 - dibromoprop-1-ene
e - 1,2 - dibromoprop-1-ene
f - } Possibly isomeric monobromopropenyl acrylates
g - }
h - 2,3 - dibromopropan-1-ol
i - } Possibly isomeric diomer of allyl acrylate type
j - }
k - 2,3 - dibromopropyl acrylate (monomer)
l - Unidentified
m - 2,3 - dibromopropyl methacrylate

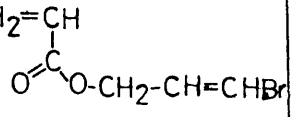
Fig.4.16. G L C trace for the degradation products of peaks 3 and 4 in the subambient T V A curve (figure 4.14) by using 5 ft. $\frac{1}{4}$ inch diameter, 10% microwax on chromosorb column isothermally at 140°C.

d. Condensable products were separated by subambient T V A as shown in figure 4.14. There are four distinct peaks. I r spectroscopy shows that the first peak contains HBr and CO_2 while peak 2 is due to allyl bromide. The mass spectrum of the material in peaks 3 and 4 is shown in figure 4.15, and a gas-liquid chromatogram in figure 4.16. A complete list of products of degradation of P 2,3-D B P A is shown in table 4.3; as before, some reference compounds were unavailable and identities of some peaks have been inferred from mass spectral data. These products are indicated by *.

Table 4.3. DEGRADATION PRODUCTS OF P 2,3-D B P A

Degradation fraction	Products	Methods of analysis
Non-condensable materials	CH_4 , CO , propene , H_2	I R & M S
Cold ring fraction	long chain fragments	I R in solution
Residue	Carbon	I R (KBr disc)
Condensable materials:		
Peak 1 (S A T V A)	CO_2 , HBr	I R & M S
Peak 2 (S A T V A)	Allyl bromide	I R & M S
Peak 3 (S A T V A)	prop-1-en-3-ol *	M S
	$CH_2 = CH - CH_2 OH$	
	monobromopropenol *	M S
	1,2 - dibromopropane	M S &g l c
	2,3 - dibromoprop-1-ene	M S &g l c
	1,2 - dibromoprop-1-ene	M S &g l c
	Isomeric monobromopropenyl acrylates *	M S

Cont'd Table 4.3.

Degradation fraction	Products	Methods of analysis
Peak 4 (S A T V A)	e.g. 	
	2,3 - dibromopropan-1-ol	M S & g l c
	Isomeric dimeric species based on allyl Acrylate *	M S
	2,3 - dibromopropyl acrylate (monomer)	M S & g l c
	2,3 - dibromopropyl methacrylate	M S & g l c

Again, the temperature ranges over which the various degradation products were evolved were identified by a stepwise degradation procedure carried out on a single sample of P 2,3-D B P A in the sub-ambient T V A apparatus. This procedure has been described earlier for P 2,3-D B P M; in this case the temperatures of the stages ranged from 240°C to 500°C, and the series of S A T V A curves obtained is shown in figure 4.17.

Peak 1 first appears at 280°C, as in the P 2,3-D B P M degradation, whereas the other three peaks are present at all stages from 240°C.

iv. Quantitative Estimation of the Degradation Products

Infra-red spectroscopic techniques were used for the quantitative study of the products in peaks 1 and 2, and g l c techniques for

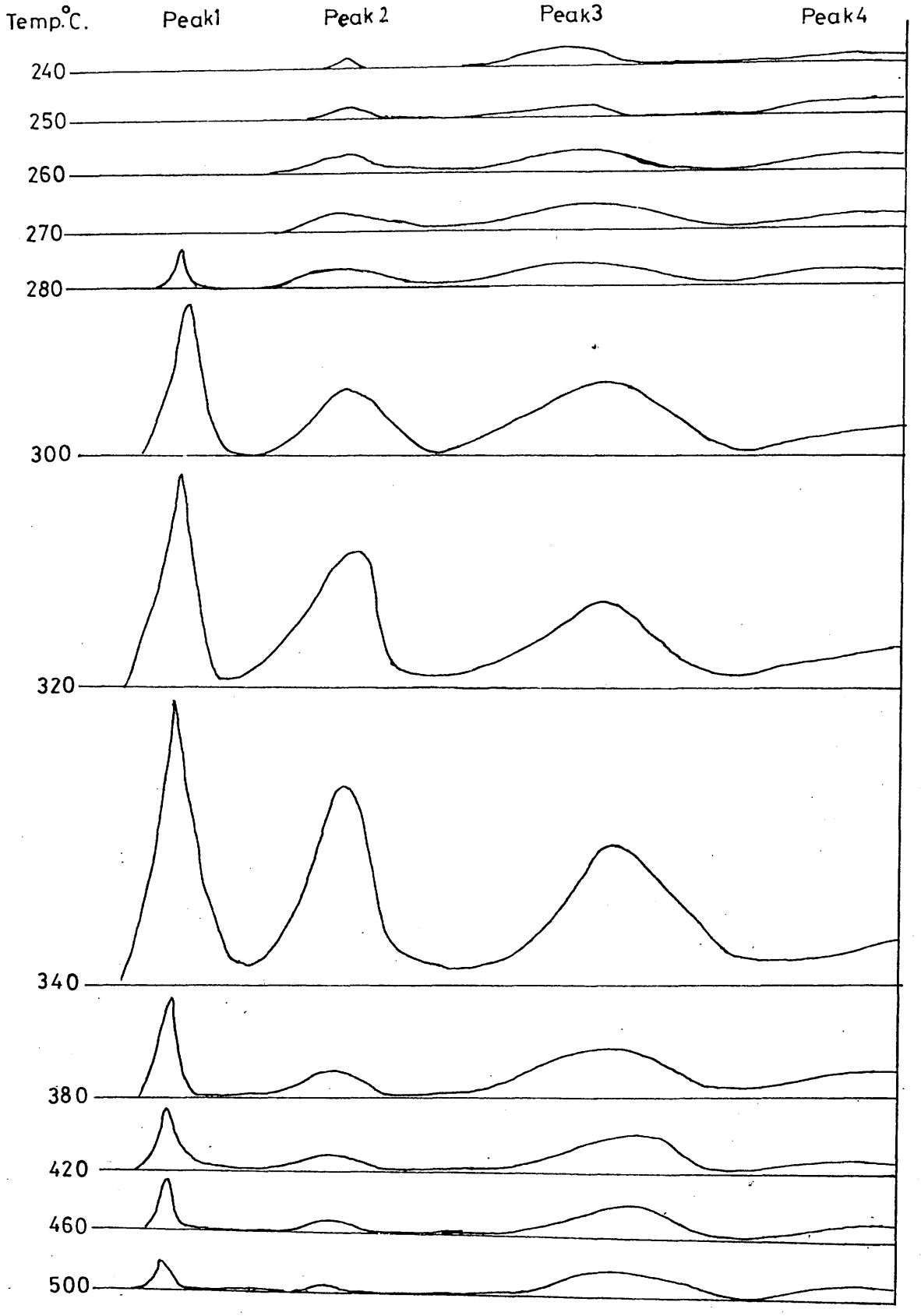


Fig. 4.17. Subambient T V A curves for degradation products of a single sample of P2,3 - D B P A (from programmed degradation under vacuum from ambient to successively higher temperature at 10°C/min, 50 mg small pieces sample size). Sample held at each temperature while products were collected for S A T V A.

the products in peaks 3 and 4. Again, in the latter case, some minor products were unavailable for calibration purposes, and estimated retention times and sensitivities were used based on boiling points and data for structurally similar compounds. These products are indicated by * in table 4.4, which gives the results for programmed degradation from ambient temperature to 500°C. Values marked * should only be regarded as qualitative.

Table 4.4. QUANTITATIVE ANALYSIS OF THE PRODUCTS OF DEGRADATION OF P 2,3- D B P A (20° - 500°C at 10°C/min)

Product	wt% of original polymer
HBr	46.0
CO_2	7.9
Propene	0.5
Allyl bromide	8.3
Prop-1-en-3-ol *	0.6 *
Monobromoprop-1-en-3-ol *	0.7 *
1,2 - dibromopropane	2.5
2,3 - dibromoprop-1-ene	3.5
1,2 - dibromoprop-1-ene	2.9
Isomeric monobromopropenyl acrylates *	3.5 *
2,3 - dibromopropan-1-ol	3.2
Isomeric dimeric species based on allyl acrylate *	1.6 *
2,3 - dibromopropylacrylate (monomer)	0.5
2,3 - dibromopropyl methacrylate	trace
C R F	14
Residue	3
Total product	98.7

4.4 DISCUSSION

In spite of the fact that the chemical structures of P 2,3 - D B P M and P 2,3 - D B P A are so similar, there is a wide divergence in their thermal degradation behaviour. This is similar to the thermal degradations of poly (n-butyl methacrylate)[19] and poly (n-propylacrylate).[20,21,22] It was observed that while poly (n-butyl methacrylate) yields appreciable amounts of monomer, the reaction is by no means quantitative. Monomer production ceases at 30-50% conversion, and at higher temperatures a complex series of reactions occurs in which there is evidence of decomposition of the pendant ester group to give products such as butene, methacrylic acid and anhydride. Grassie and Grant[23] studied the thermal degradation of poly (tert-butyl methacrylate) and it seems to be generally agreed that the ester decomposition reaction proceeds by a molecular mechanism involving interaction between the carbonyl group and hydrogen atoms of the carbon atoms of the ester group. Grassie[24] drew attention to the importance of β - hydrogen atoms in facilitating ester decomposition at the expense of depolymerisation. He suggested that the ester decomposition only becomes important when the monomer unit incorporates five β-hydrogen atoms and depolymerisation is quantitative when there are at most one or two β-hydrogen atoms.

The behaviour of the poly(acrylates) as a group was also recognised to be more complex than originally envisaged. More careful analysis revealed ester decomposition products like carbon dioxide and the corresponding olefines and alcohols as well as traces of monomer. But clearly there is some considerable overlap in the thermal degradation behaviours of P 2,3 - D B P M and P 2,3 - D B P A homopolymers.

In the light of the experimental results, a number of interesting conclusions may be drawn :

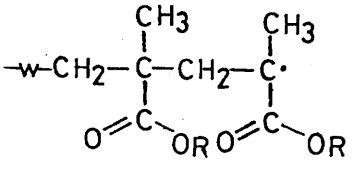
i. T_{max} for P 2,3-D B P M and P 2,3-D B P A are lower than for (P M M A) and (P M A) respectively. This relative instability, at least in the methacrylate, may be due to the steric effect of the brominated bulky side group in facilitating depolymerisation.

ii. Carbon - bromine bonds on the side chain readily undergo scission, which did not occur in the thermal degradation of poly (2-bromoethyl methacrylate)[25].

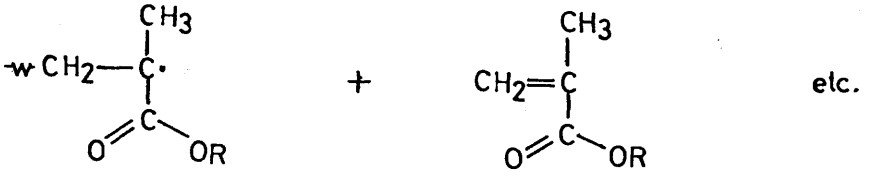
In discussing the detailed reaction mechanisms which may account for the observed degradation products, it is convenient to consider the homopolymers separately.

1 - P 2,3-D B P M

The dominant degradation product (55.8%) is monomer, and this reflects the general characteristic mode of polymethacrylate degradation observed by Grassie[19]. A long chain polymer **radical of the form**

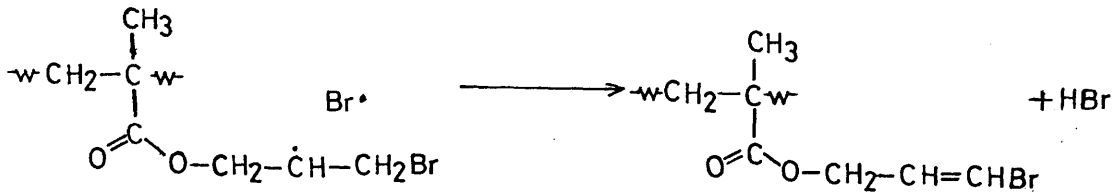


is formed either by random chain scission or by initiation at an unsaturated chain end; this radical then "unzips" to produce monomer and a similar radical, and repetition of the process can give high yields of monomer.



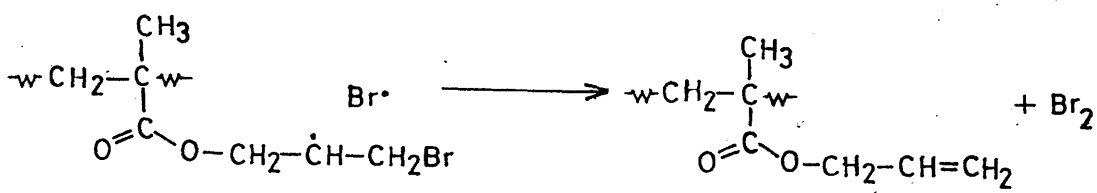
Initiation at unsaturated chain ends is normally observed at lower temperatures than random scission, and is detected as a shoulder on the main T V A peak. It is absent in this case, but this is not surprising in view of the fairly high molecular weight (443,000) of the polymer, which greatly reduces its importance. The other major volatile product is HBr (12.2%), which, as already mentioned, is not an important product in the degradation of poly (2-bromoethyl methacrylate). Clearly the simplest side-chain reaction involves the scission of a C-Br bond, with the production of a Br atom. This Br atom may undergo any one of four subsequent reactions.

a. It may abstract an H atom from an adjacent carbon atom, leaving a double bond in the side chain.



monobromopropenyl methacrylate unit

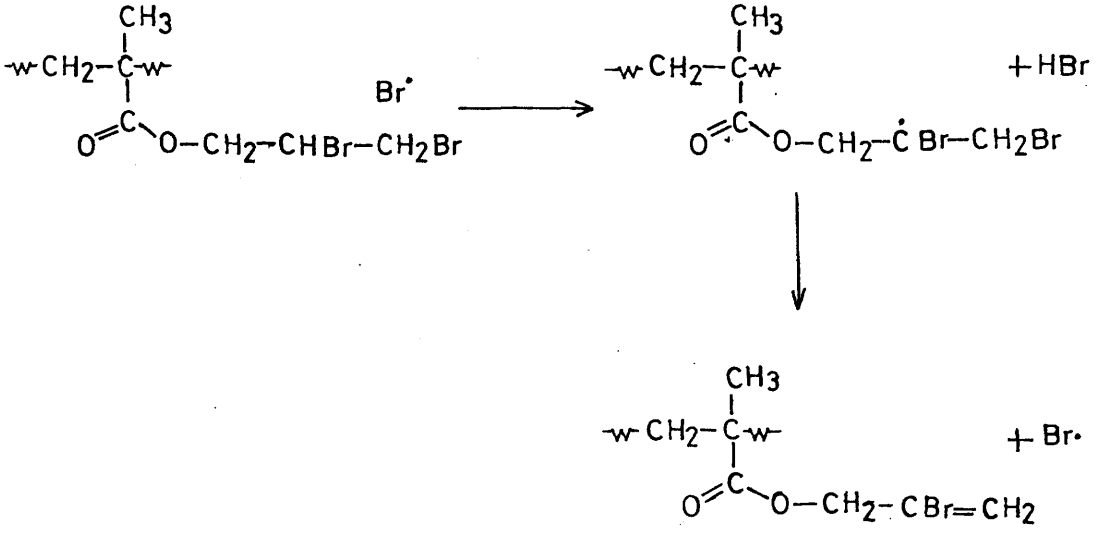
b. It may abstract a second Br atom from the adjacent carbon atom, forming a Br_2 molecule (3.1% of products) and leaving a double bond in the side chain.



allyl methacrylate unit

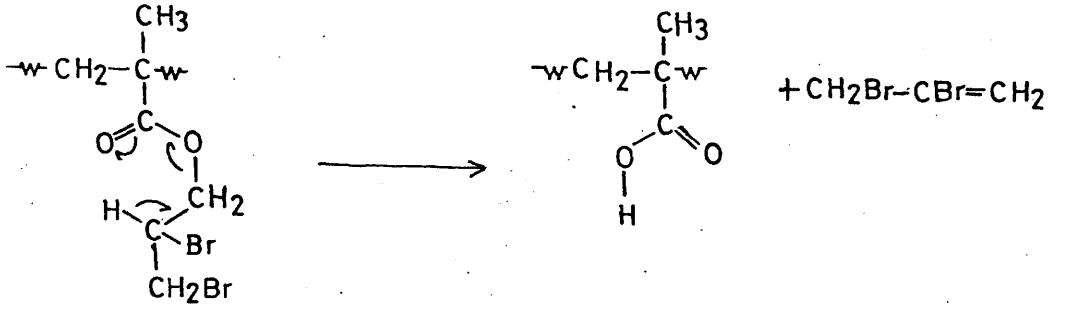
c. Two Br atoms may react to form a Br_2 molecule.

d. The Br atom may abstract a H atom from the side chain of another monomer unit, forming HBr and leaving a side chain radical which can stabilise by ejecting a Br atom.

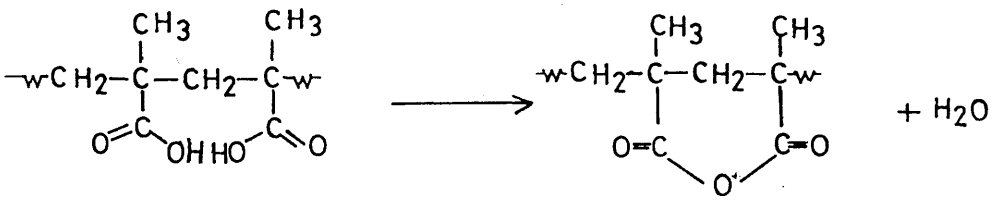


The modified monomer units left after process (a), (b) and (d) indicate clearly possible sources of allyl mathacrylate and the isomeric monobromopropenyl methacrylates which together account for approximately 3.9% of the products.

The process of ester decomposition in poly (methacrylates) which have β-hydrogen atoms in the side chain is also well known.[24] The initial products are a methacrylic acid unit and an alkene.

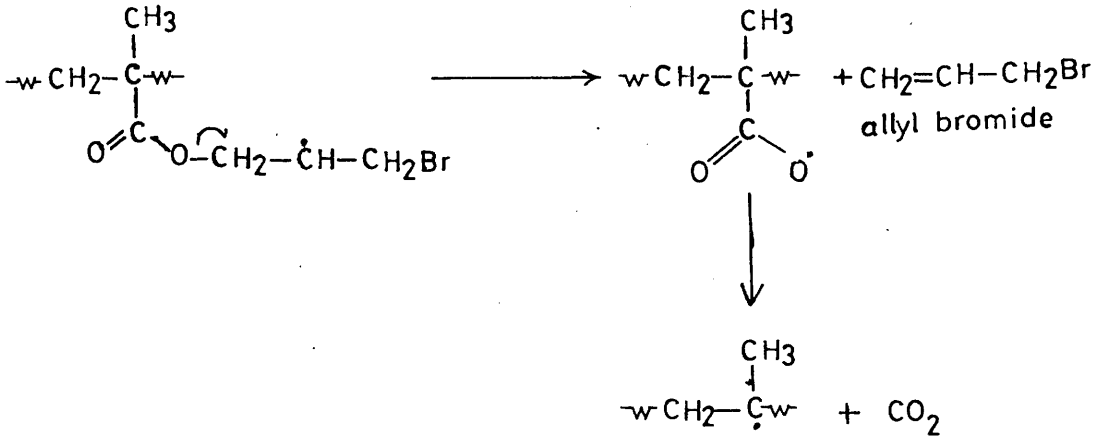


If two adjacent units react in this way, water may be eliminated between the two acid groups at higher temperature to yield a methacrylic anhydride linkage.[26]

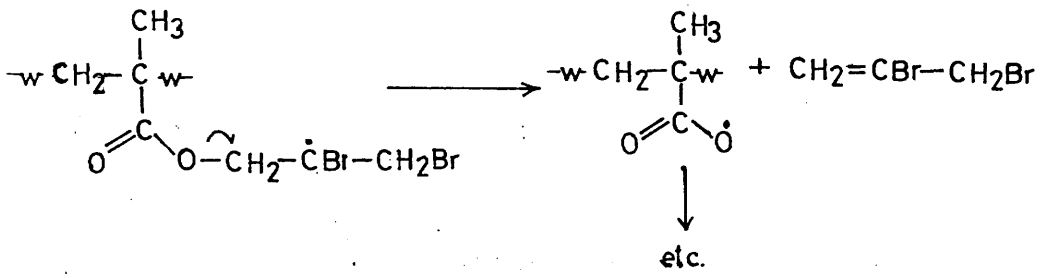


The i r spectrum of the cold ring fraction indicates the presence of some anhydride structures superimposed on a basic structure which shows growing unsaturation and some similarities to the original polymer. The small amount of the two products deriving from this process, water and the dibromopropene, indicate, however, that ester decomposition is a relatively minor process in this case. Again, this is not surprising in view of the fact that the side chain contains only one β-hydrogen atom. However, its occurrence to a small extent is confirmed by the presence of a trace of methacrylic acid among the products; this can arise when an unzipping reaction passes through an isolated methacrylic acid unit.

Of the products not so far discussed, CO_2 (2.6%) and allyl bromide (2.5%) are the most significant. The production of equimolar amounts of these products could be satisfactorily explained by a mechanism of the following type, which follows the initial ejection of a Br atom from the side chain, as discussed earlier in connection with the formation of HBr.



This reaction could also be a secondary source of the dibromopropene observed as a minor product; following intermolecular hydrogen abstractionby a Br atom, a reaction analogous to that given above can occur.

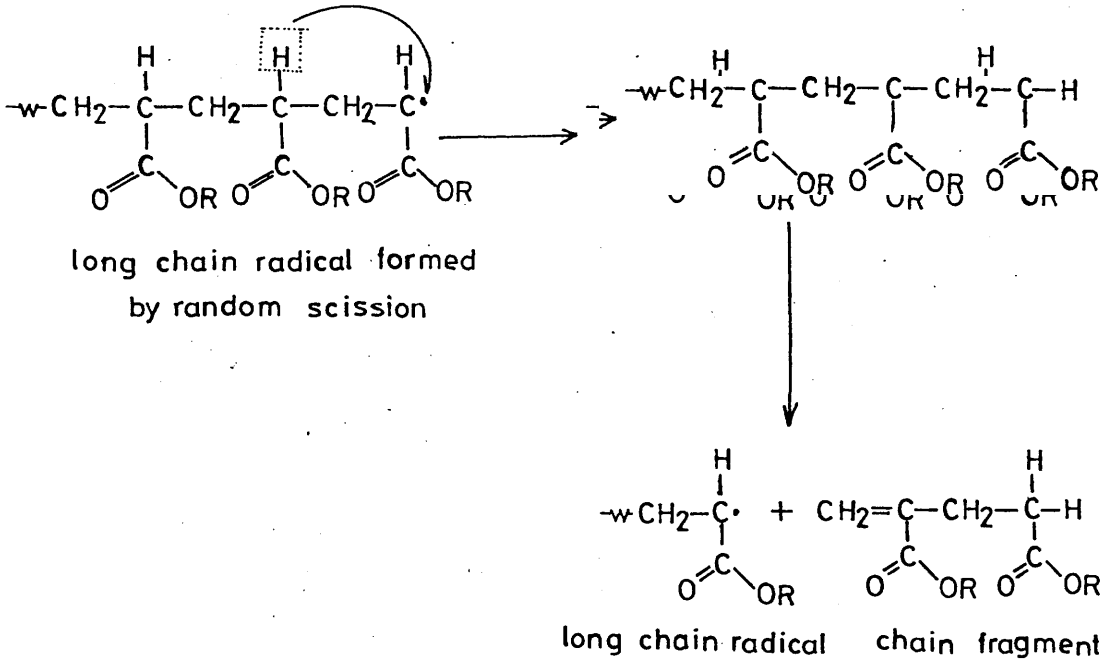


In fact, the molar ratio CO_2 : allyl bromide observed is nearer to 3:1; the additional CO_2 can, however, be formed readily by the decomposition of methacrylic acid or anhydride units unable to volatilise as short chain fragments, leaving behind the carbonaceous char. Of the other minor products, propene (0.2%) presumably arises from fragmentation of chain structures such as the one remaining above after elimination of CO_2. 1,2 - Dibromopropane (0.2%)

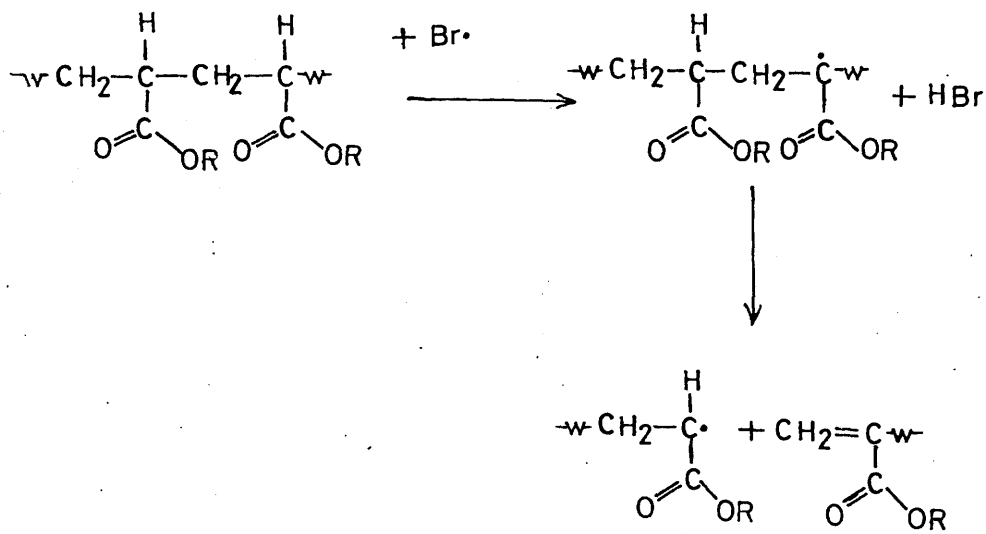
can be formed if the $O-CH_2-CH\,Br-CH_2Br$ bond undergoes scission, followed by hydrogen abstraction by the resulting alkyl radical.

2 - P 2,3 - D B P A

The notable features of the degradation products from this polymer as compared with those from the corresponding methacrylate are the much higher yield of HBr (46.0%), the increased yields of CO_2 (7.9%) and allyl bromide (8.3%), the increased yield of cold-ring fraction (14%) and the virtual absence of monomer. In this case, therefore, the mechanism of degradation will be dominated by side-chain reactions and chain-transfer to give short chain fragments, rather than the unzipping reaction to produce monomer typical of poly (methacrylates). This general difference has long been established;[27,28] the poly (methacrylate) chain radical is stabilised by its methyl and carboxyl substitutes and yields monomer, while the poly (acrylate) chain radical is much more reactive, and abstracts a tertiary hydrogen atom from the chain (inter- or intra-molecularly) to give rapid chain scission and small chain fragments.



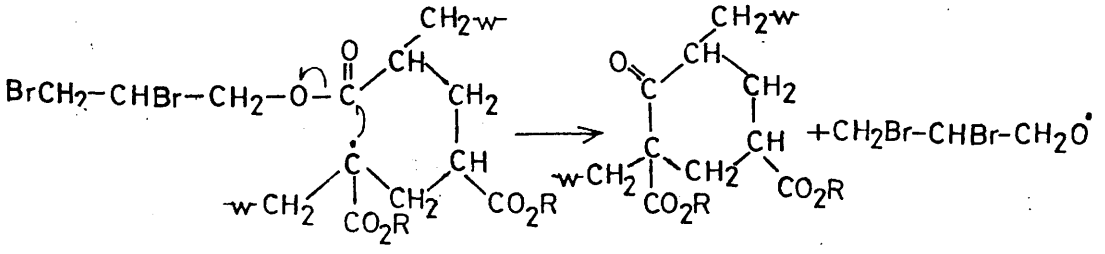
The mechanisms leading to the formation of HBr are probably similar to those already proposed for P 2,3-D B P M; namely, elimination of a Br atom followed by hydrogen abstraction. In this case, in addition to intramolecular abstraction of an H atom from an adjacent carbon atom in the side chain (leading to the formation of isomeric monobromopropenyl acrylate units in the chain) or intermolecular abstraction of an H atom from the side chain of another unit (leading to the same monobromopropenyl acrylate units after ejection of a Br atom), a third hydrogen abstraction process is possible. The tertiary C-H bond is weak, and abstraction of this hydrogen by a bromine atom leads to chain scission followed by further formation of small chain fragments or transfer.



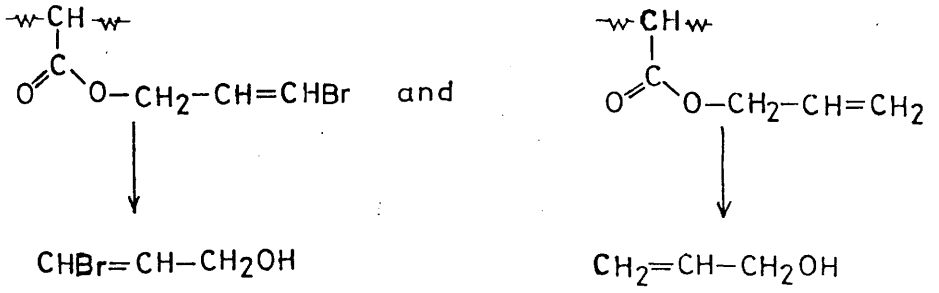
This type of process can add to the chain fragments formed by the alternative process of random scission and transfer. The yield of HBr is much higher in the acrylate degradation than in the methacrylate degradation because the competing reaction of monomer production

(which removes unreacted side chain from the system) is absent in the acrylate case.

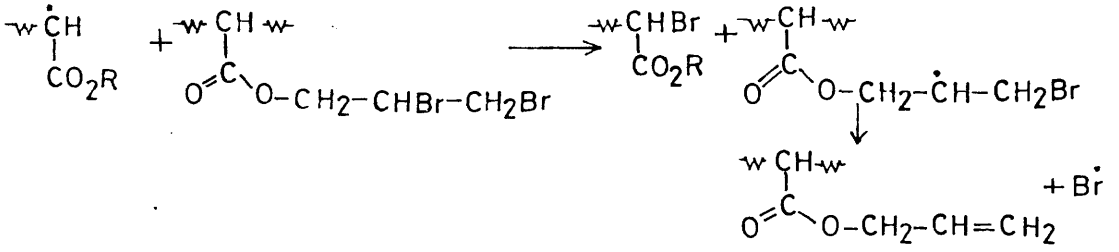
The mechanisms resulting in the formation of Allyl bromide, CO_2, dibromopropenes, propene and 1,2 dibromopropane are identical to those already presented in the discussion of the degradation of P2,3-D B P M. The chain fragments in this case do not exhibit i r absorptions typical of anhydride structures, and it is possible, therefore, that ester decomposition is of little importance in this reaction. A significant amount (3.2%) of 2,3-dibromopropan-1-ol is formed and there is mass spectral evidence for the formation of smaller amounts of monobromoprop-1-en-3-ol and prop-1-en-3-ol. The formation of 2,3 - dibromopropan-1-ol is readily explained by a mechanism analogous to that proposed for poly (n-alkylacrylates) by Grassie et al[21], commencing with a long chain radical of the type



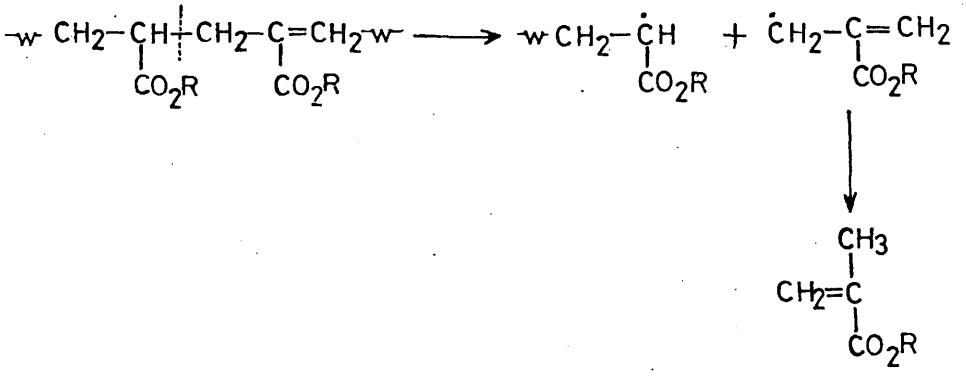
The alkoxy radical formed, by abstracting an H atom from elsewhere in the polymer, can readily yield CH_2Br CH Br CH_2OH. Alternatively, one of the mechanisms proposed by Cameron and Kane[27] may be responsible for the production of the alkoxy radical, since there is slight evidence of a shoulder at 1760 cm^{-1} in the i r spectrum of the cold ring fraction which may be due to a lactone structure. The monobromopropenol and propenol can be formed by an analogous mechanism from units containing the partially reacted side chains shown below.



The first structure has been encountered earlier during the discussion of HBr formation; the allyl acrylate structure of the second example is most readily approached by a route involving Br atom abstraction by a long chain acrylate radical followed by ejection of the other Br atom to stabilise the side chain by formation of a double bond.



In addition to the mass spectral evidence for the presence of the propenol, this type of reaction is further supported by mass spectral evidence of a dimeric species based on the allyl acrylate structure. The trace of 2,3-D B P M monomer formed is most readily accounted for in terms of a reaction at an unsaturated chain end.[24,29] Scission of the allylic C-C bond followed by H abstraction readily yields the required product.



CHAPTER 5

THERMAL DEGRADATION of 2,3 - D B P M - M M A and 2,3 - D B P A - M M A COPOLYMERS

5. 1 INTRODUCTION

The principal degradation reaction which occurs in P M M A[30,31] is depolymerisation to monomer in high yield. This chapter will describe the effect of the comonomers 2,3 - D B P M and 2,3 - D B P A, on the products of degradation both qualitatively or quantitatively. The stability of these copolymers will also be discussed, and finally their degradation mechanisms. Five copolymers with different compositions were prepared from each pair by the methods outlined in Chapter 2.

5. 2 THERMAL DEGRADATION of 2,3 - D B P M - M M A COPOLYMERS

i. Molecular Weights

The 2,3 - D B P M - M M A copolymers contain 71.5% (A_1) , 60% (A_2) , 32% (A_3) , 10% (A_4) and 5% (A_5) of 2,3 - D B P M units. The Number Average Molecular Weights were measured by the method described in Chapter 2 and are listed in table 5. 1. As the M M A content is increased the molecular weight obviously decreases.

Table 5. 1. Number Average Molecular Weights of 2,3 - D B P M - M M A Copolymers

2,3 - D B P M - M M A	No. Average Molecular Weight $\overline{M}_n$
A_1	1,100,000
A_2	618,000
A_3	590,000
A_4	538,000
A_5	404,000

ii. Thermal Volatilisation Analysis, (T V A)

Powder samples (50 mg) were heated from ambient temperature to 500°C at 10°C/min under normal TVA conditions. The T V A traces for copolymers A_1 , A_2 , A_3 , A_4 and A_5 are shown in figures 5.1 , 5.2 , 5.3 , 5.4 and 5.5 respectively. There are two distinct peaks, the relative sizes changing with copolymer composition. Volatilisation starts between 190° - 200°C. The T_{max} of the first peak occurs between 290° - 330°C and for the second stage, in the region of 400° - 410°C. At higher methyl methacrylate contents the first stage of degradation is characterised by significant formation of a high boiling fraction (condensed in the 0°C trap) and traces condensed in the other traps. In the second stage, the separation of the curves shows that there are products with a wide range of volatilities and a considerable amount of material is non-condensable at -196°C. A substantial cold ring fraction was coloured deep yellow and was dissolved in chloroform for infra-red spectroscopic analysis. A small amount of black residue (4 - 2%) remains at 500°C.

iii. The Stability of 2,3 - D B P M - M M A Copolymers

Grassie et al[32], compared the stabilities of VA - VC copolymers using the T V A technique. Figure 5.6 shows the initial stage of the 0°C T V A trace of the various 2,3 - D B P M - M M A copolymers as well as of P M M A and P 2,3 - D B P M homopolymers. Although the Pirani response is a measure of rate of volatilisation, the relation between rate and Pirani response[9] is only linear up to pressures of the order 10^{-2} torr (approximately 2 m v output on the commercial Pirani gauge employed) thereafter becoming non-linear. Figure 5.7 presents a comparison of rates of volatilisation at 260°C as measured

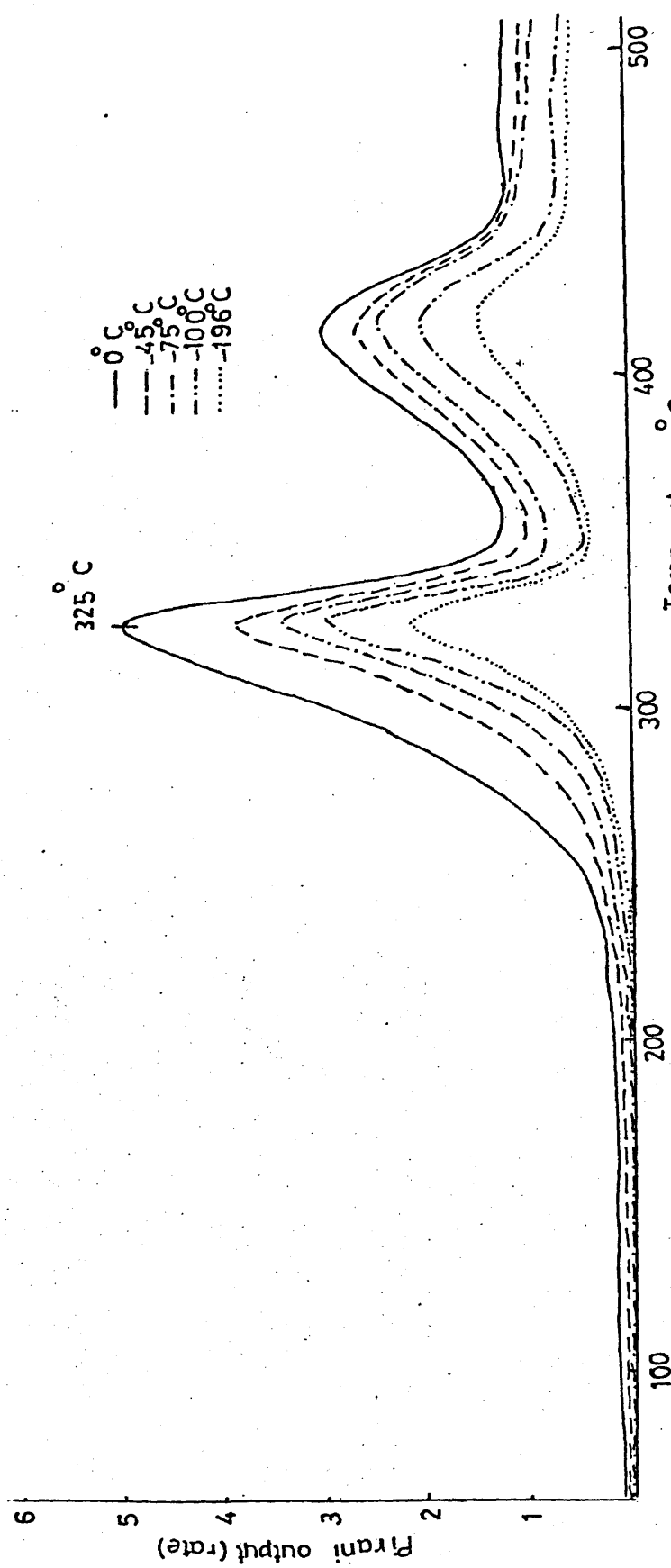


Fig.5.1. T V A curve for A_1 copolymer, sample size 50 mg ; heating rate 10^{o}C/min.

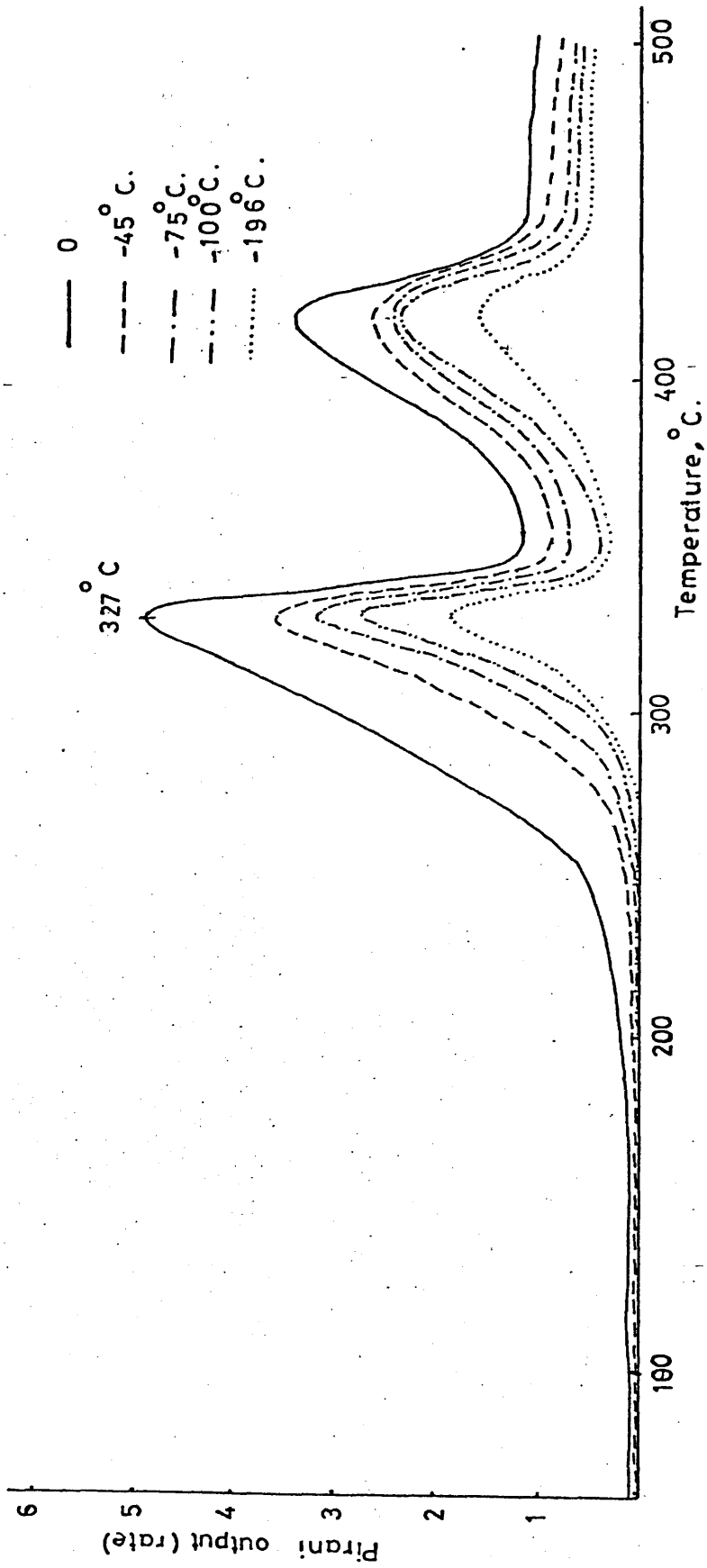


Fig.5.2. T V A curve for A_2 copolymer, sample size 50 mg ; heating rate 10^{o}C/min.

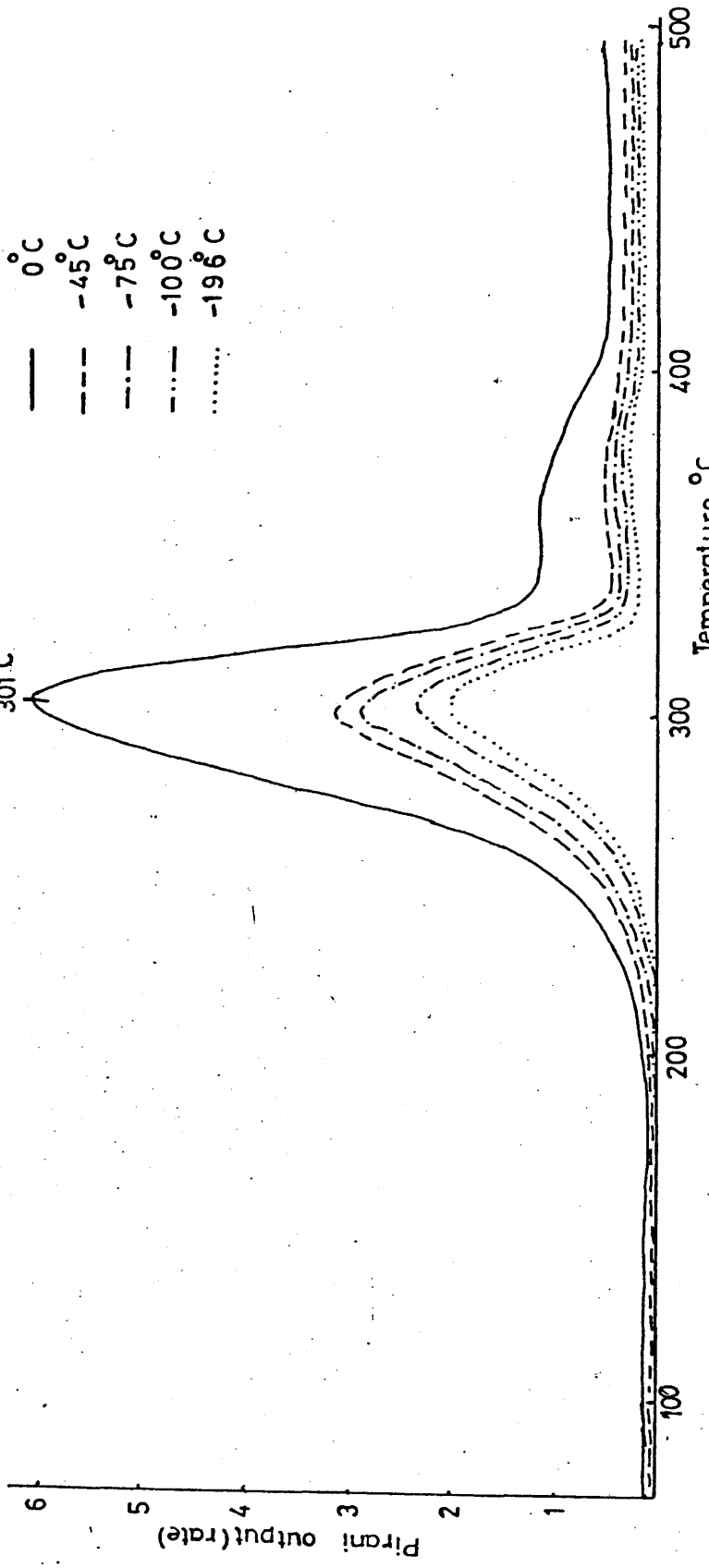


Fig.5.3. T V A curve for A_3 copolymer, sample size 50 mg ; heating rate $10^{o}C$/min.

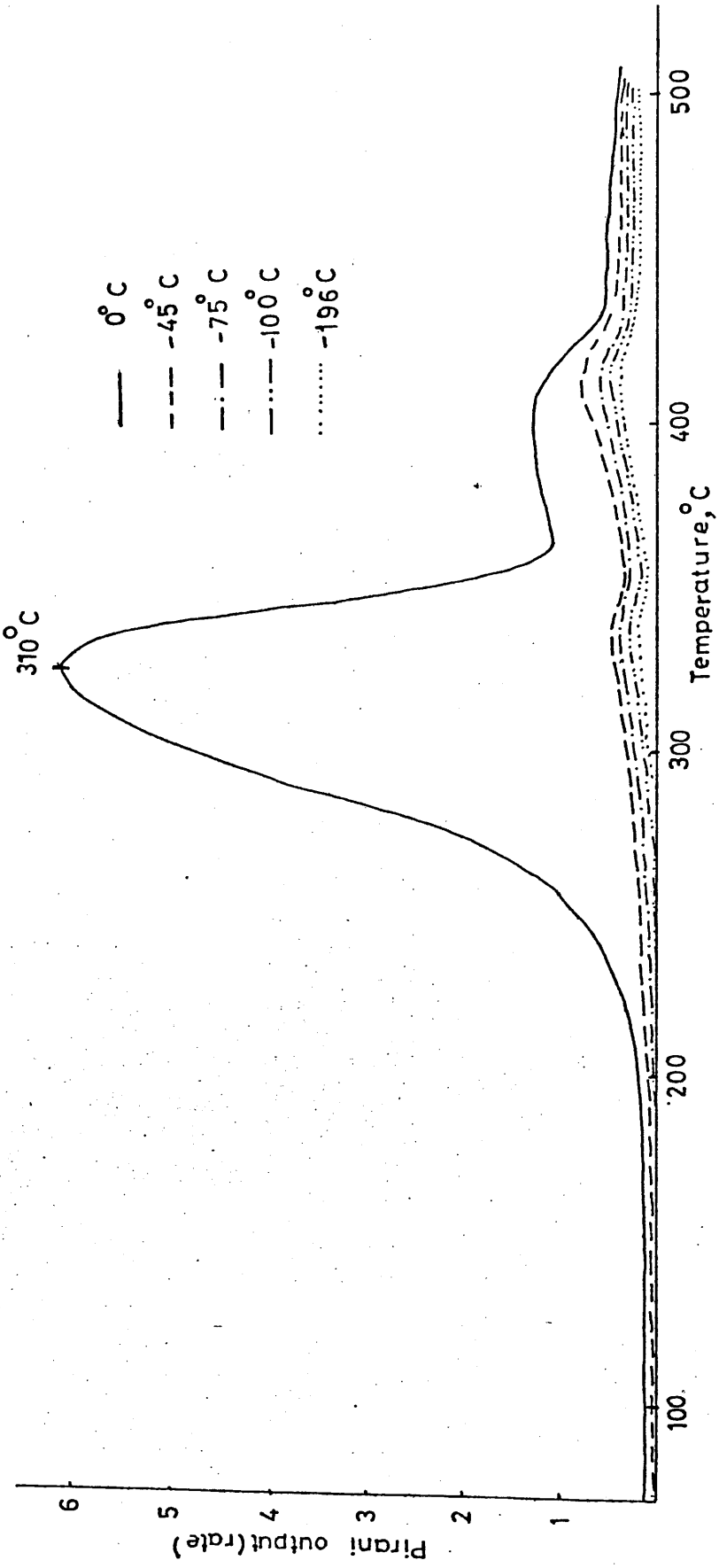


Fig.5.4. T V A curve for A_4 copolymer, sample size 50 mg ; heating rate $10^{\circ}C$/min.

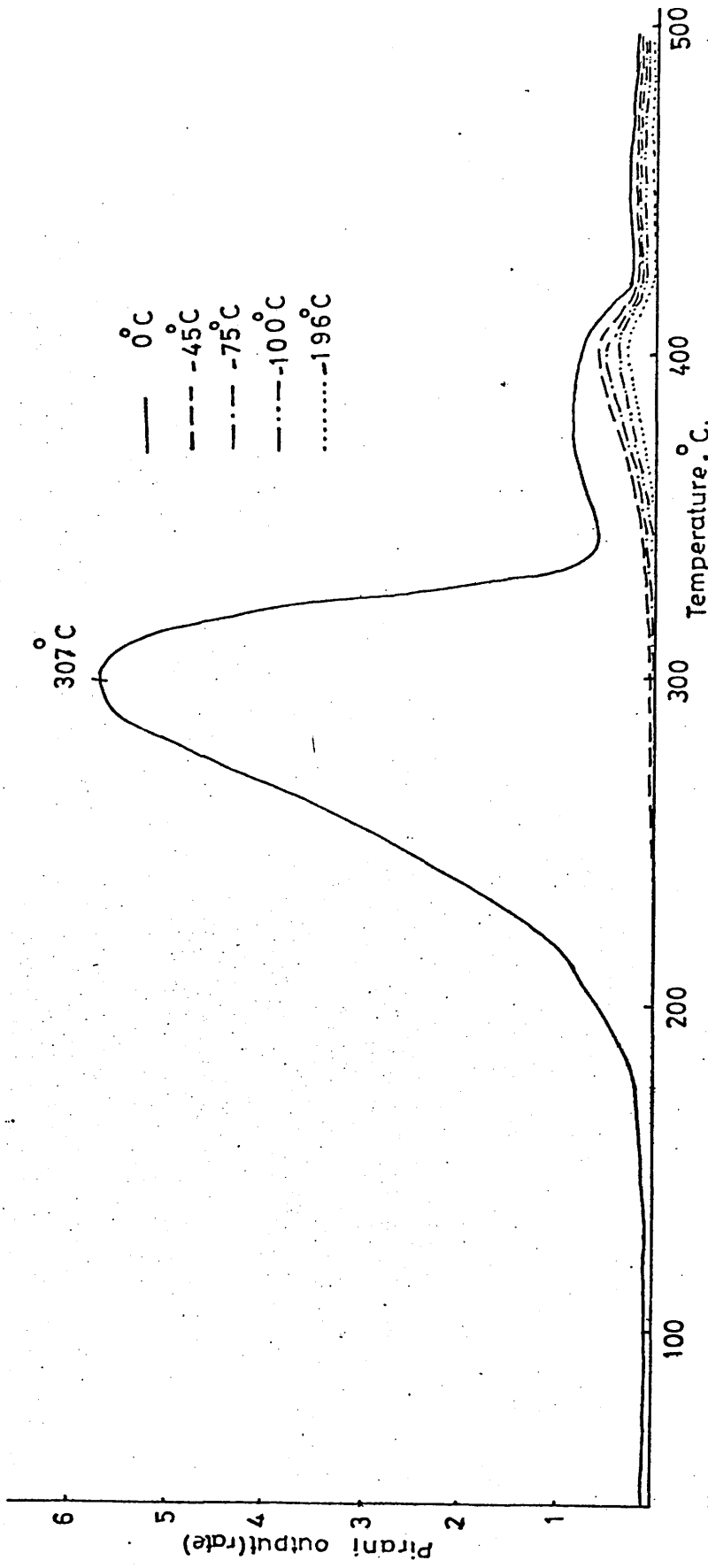


Fig.5.5. T V A curve for A_5 copolymer, sample size 50 mg ; heating rate $10^{o}C$/min.

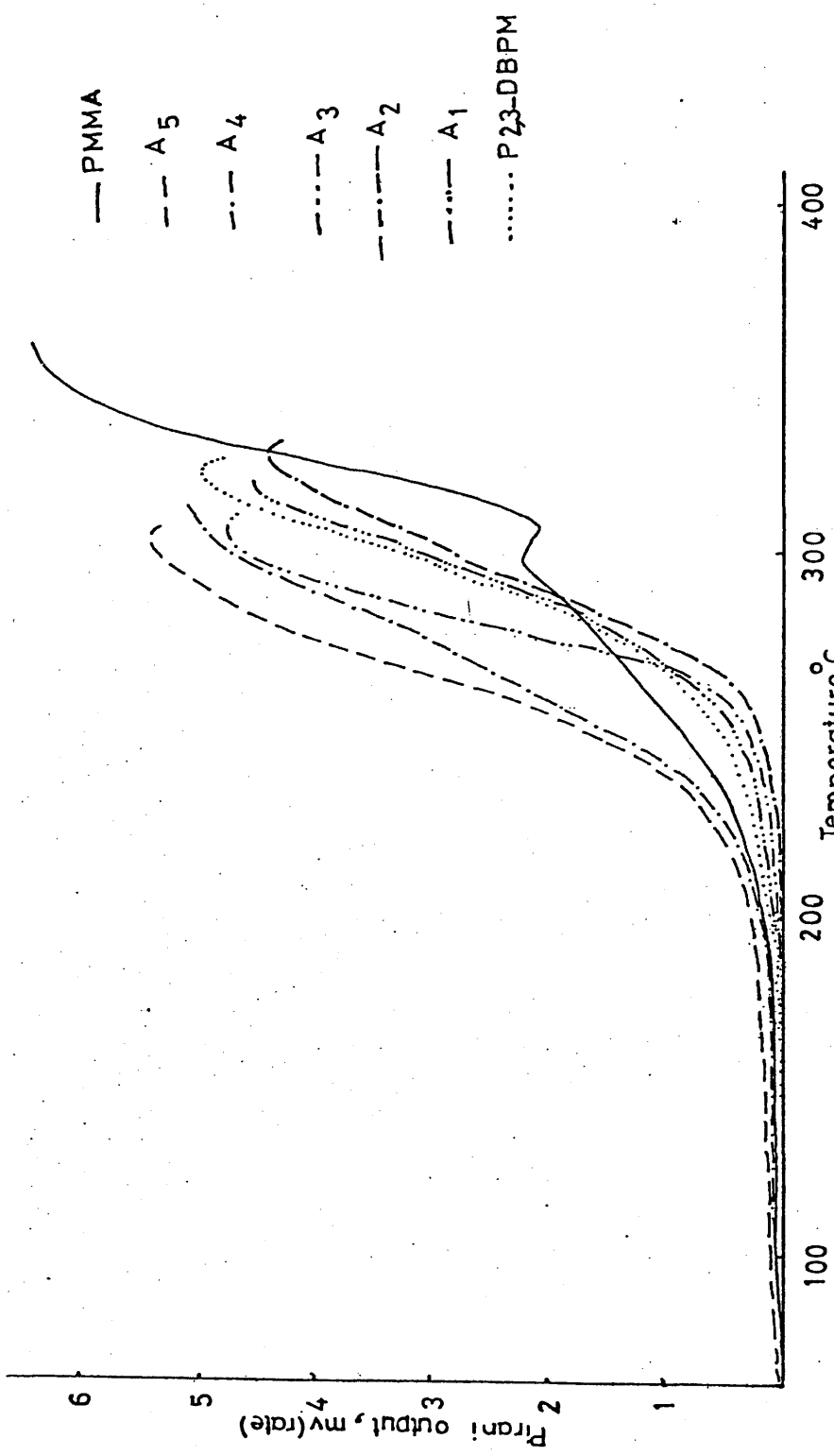


Fig.5.6. Initial stages of T V A thermograms of 2,3 - D B P M - M M A copolymers at 10^{o}C/min heating rate, 50 mg sample size.

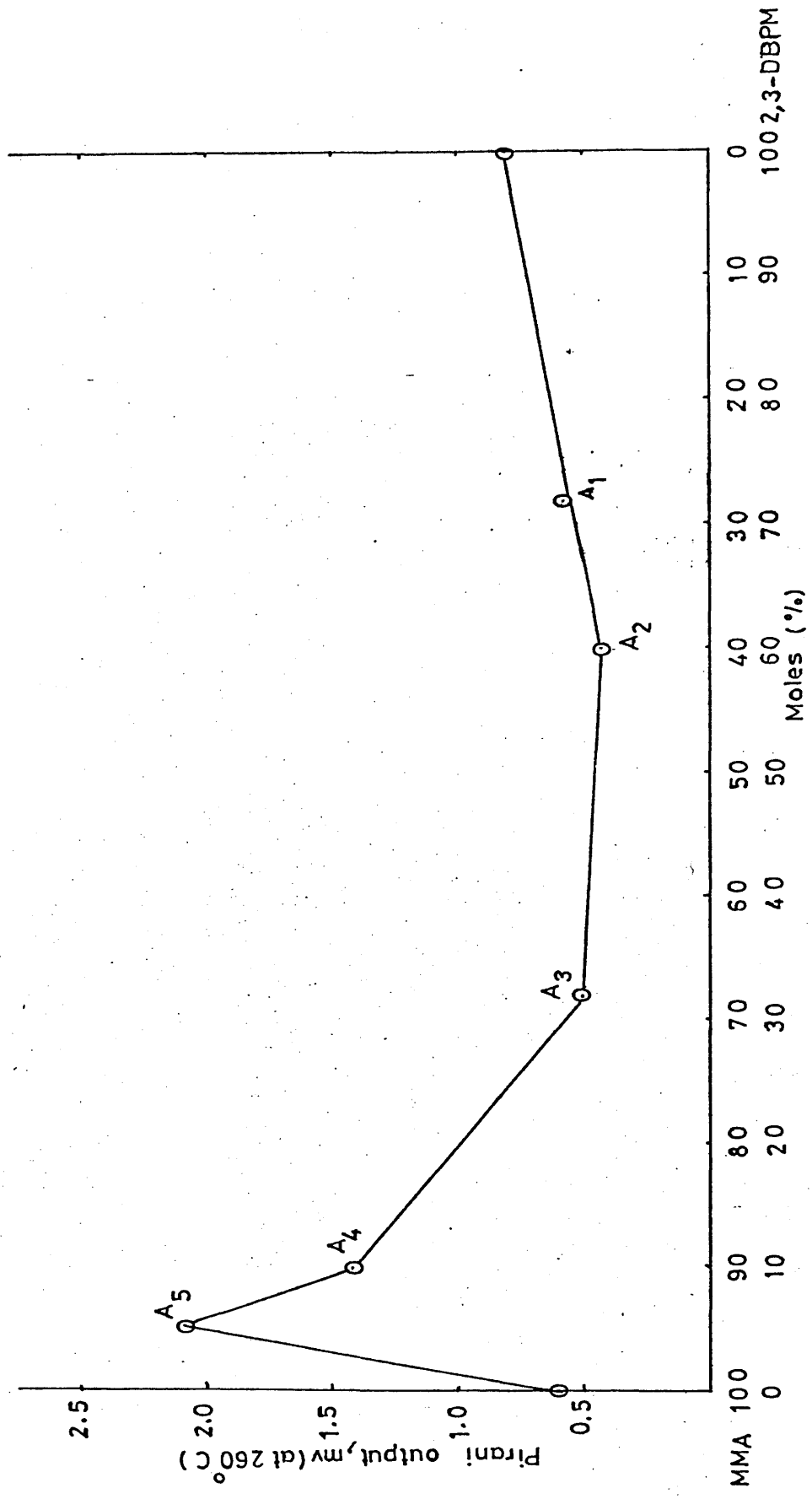


Fig. 5.7. Comparison of rate of volatilisation at 260°C as measured by Pirani reading, with copolymer composition, for heating rate 10°/min and sample size 50 mg.

by Pirani reading, as a function of copolymer composition, and shows that there is a maximum in stability near the middle of the composition range. Since the reactivity ratios for the 2,3 - D B P M - M M A system are nearly the same the copolymer is highly alternating and it thus appears that the maximum stability is achieved when most monomer units are flanked by those of the other type. The reason for this will be discussed later in this Chapter.

iv. T G and D S C

The weight loss curves for A_1 , A_2 , A_3 , A_4 , A_5 , P M M A and P 2,3 - D B P M are illustrated in figure 5.8. The weight loss under nitrogen begins in the temperature range 190° - 200°C and a two stage process is indicated, the relative importance of each stage being dependent on the copolymer composition.

Table 5. 2 shows the percentage weight loss of each polymer and T_{max}, obtained by derivative equipment associated with the T G apparatus.

Table 5. 2. Weight Loss and T_{max} of 2,3 - D B P M - M M A Copolymers

Polymer	First Stage		Second Stage		wt% remaining at 500°C
	T_{max}, °C	wt. loss, %	T_{max}, °C	wt. loss, %	
P2,3 - D B P M	325	85	400	4	12
A_1	322	86	405	10	4
A_2	327	49	430	41	10
A_3	330	72	405	25	3
A_4	330	85	420	10	4
A_5	332	87	415	4	1
P M M A	375	98	-	-	2

Figure 5.9 demonstrates the relationship between copolymer composition and percentage weight loss at 300°C as measured by the T G curves. From figures 5.7 and 5.9, it is clear that copolymer A_2 is more stable than any other copolymers and even than P M M A homopolymer.

D S C curves for A_1 , A_2 , A_3 , A_4 and A_5 are illustrated in figure 5.10. Two endothermic peaks are clearly visible, again, their relative importance being dependant upon copolymer composition. The glass transition temperatures, T_g, of the copolymers are shown by the D S C curves to be in the region of 100°C (Table 5. 3). It is clear that T_g decreases as the 2,3 - D B P M content of the copolymers is increased.

Table 5. 3. T_g for 2,3 - D B P M - M M A Copolymers

Polymer	T_g , °C
P2,3 - D B P M	-
A_1	108
A_2	108
A_3	120
A_4	125
A_5	130
P M M A	135

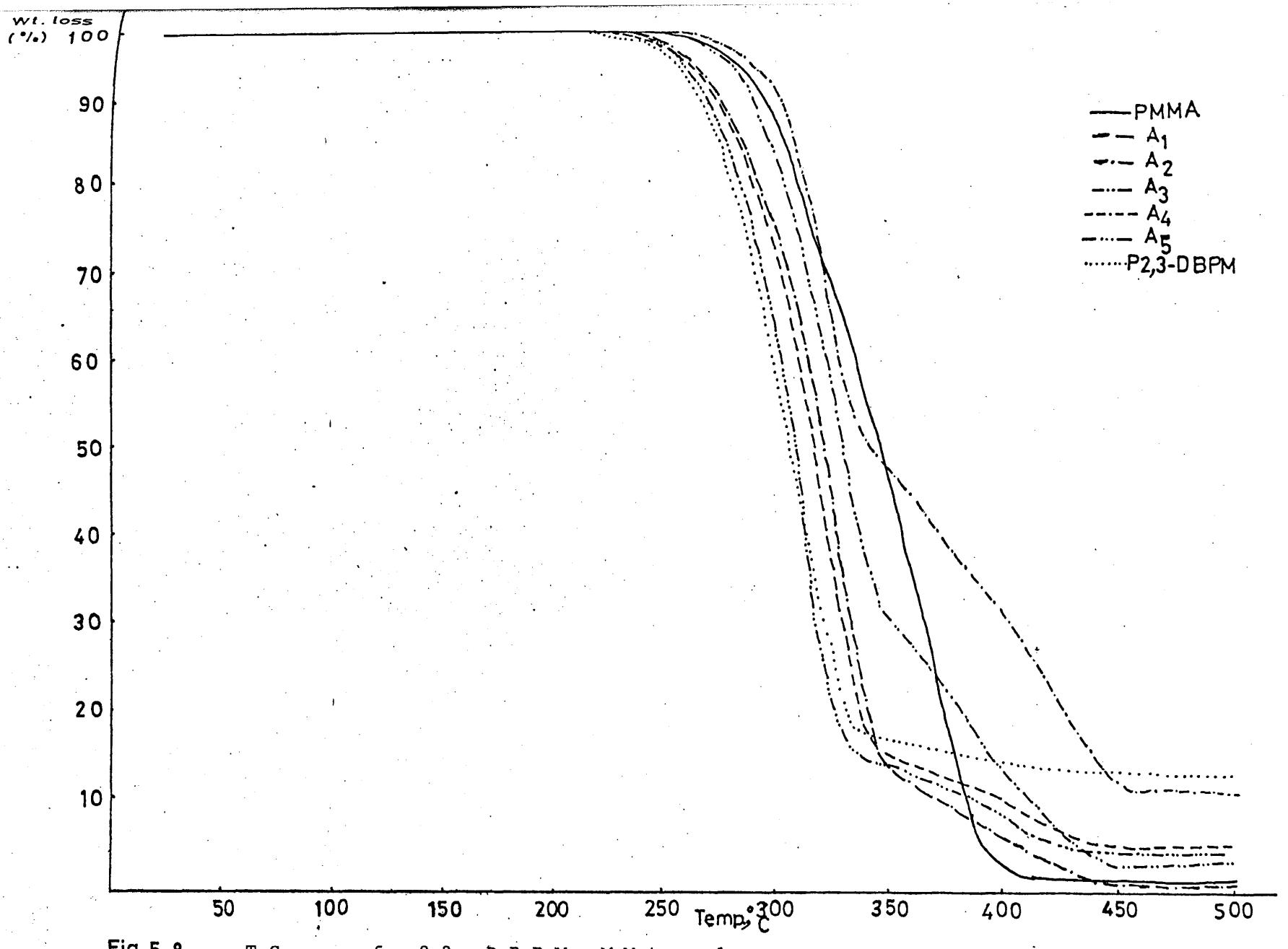


Fig. 5.8. T G curves for 2,3 - D B P M - M M A copolymers.

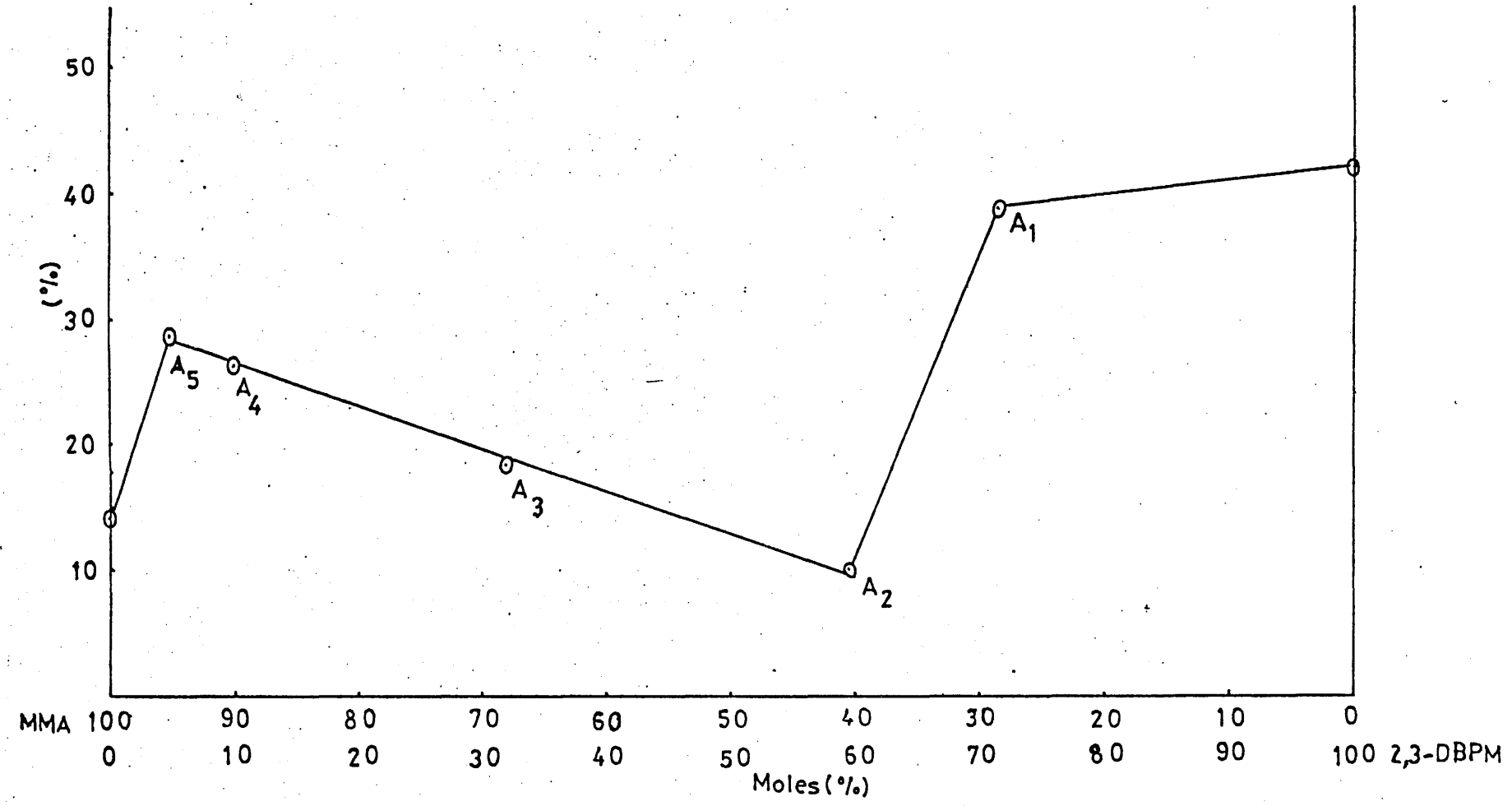


Fig.5.9. Comparison of percentage weight loss at 300°C as measured by T G curves with copolymer composition, for heating rate 10°/min.

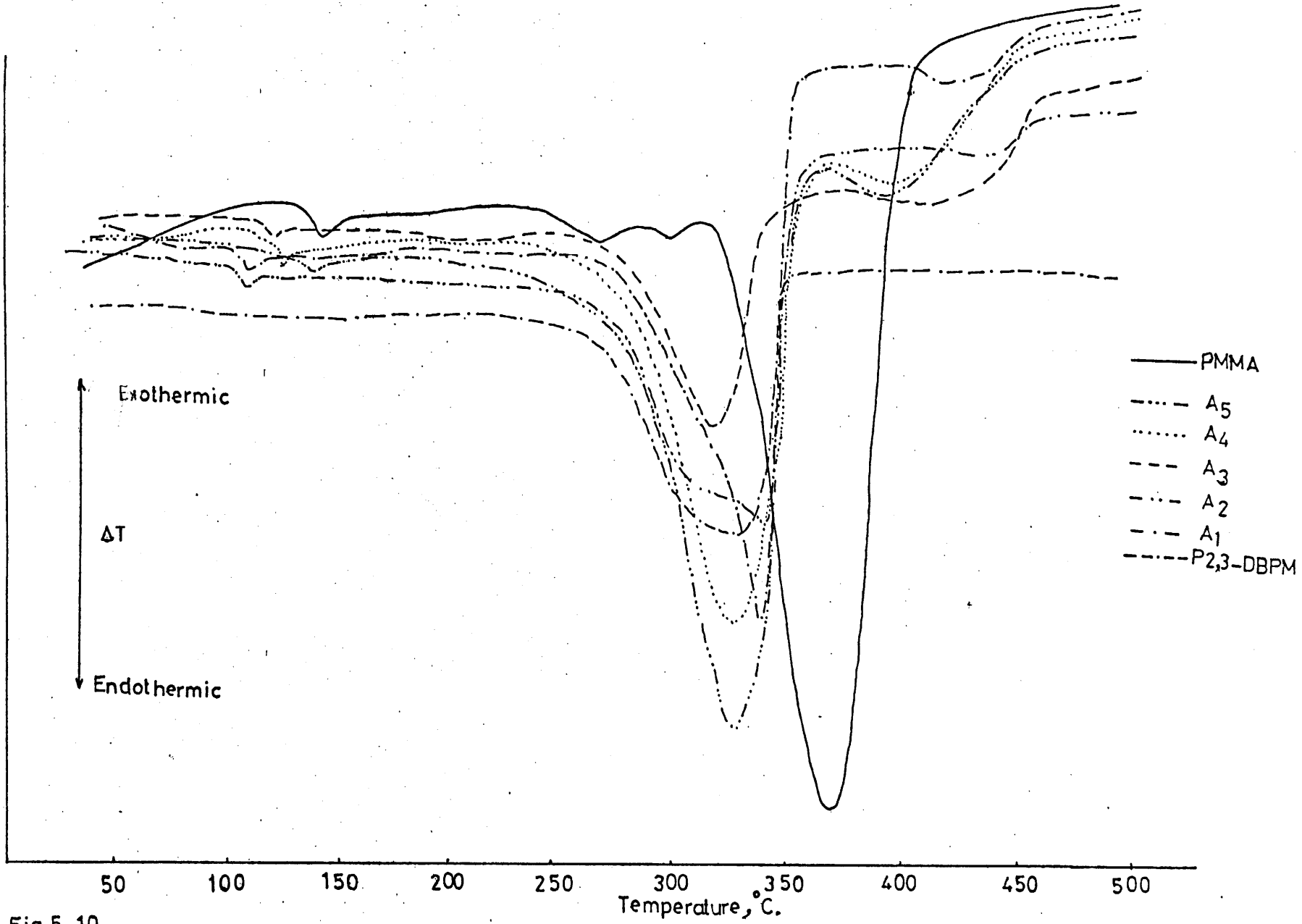


Fig.5.10. D S C curves for 2,3 - D B P M - M M A copolymers.

v. Subambient T V A and Product Analysis

Subambient T V A was carried out (as described in Chapter 2) using 50 mg of the copolymer samples. Figure 5.11 shows a typical subambient T V A trace, which exhibits seven peaks. The condensable volatile products were examined by infra-red spectroscopy and mass spectra.Non-condensables were also studied by these techniques, following degradation of the copolymer in a closed system. The liquid products were examined by g l c and mass spectra. Figures 5.12 , 5.13 , 5.14 , 5.15 , 5.16 and 5.17 illustrate i r spectra, mass spectra and a g l c trace of the degradation products recorded in the S A T V A trace (figure 5.11) of copolymer A_3. The products of degradation are recorded in Table 5. 4.

Table 5. 4. Products of Degradation of 2,3 - D B P M - M M A Copolymers

Product fraction	Products	Methods of Analysis
Non-condensable materials	CO , methane and propene	i r and mass spectra
Cold ring fraction	poly (methacrylic anhydride)	i r in solution
Residue	Carbon	i r (K Br disc)
Peak 1 (S A T V A)	H Br and CO_2	i r and mass spectra
Peak 2 (S A T V A)	CH_3Br	i r and mass spectra
Peak 3 (S A T V A)	Allyl bromide	i r and mass spectra
Peak 4 (S A T V A)	MeOH	i r , mass spectra and g l c
Peak 5 (S A T V A)	MMA , Br_2 and H_2O	mass spectra and g l c

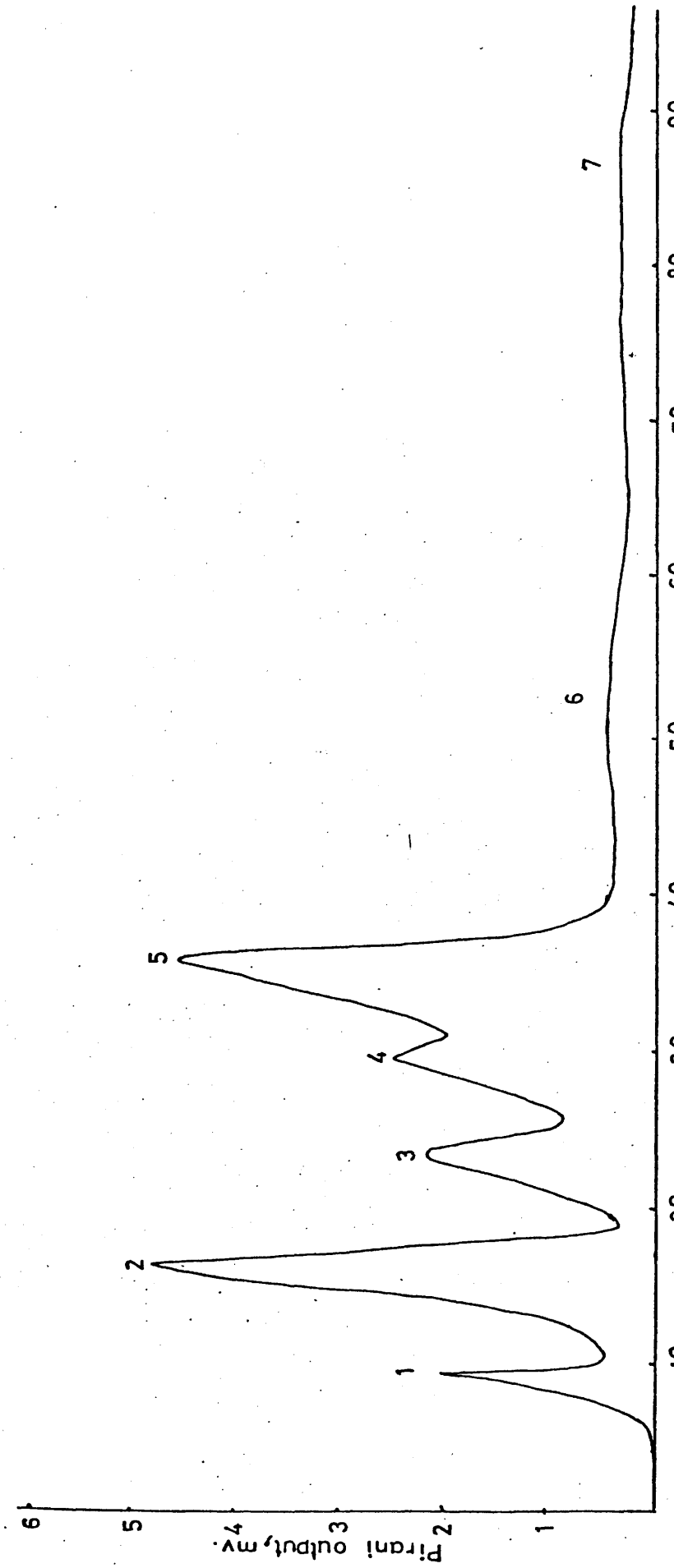


Fig.5.11. Subambient T V A curve for degradation products of 2,3 - D B P M - M M A (A_3) copolymer, (from programmed degradation under vacuum to 500°C at 10°/min , 50 mg sample size).

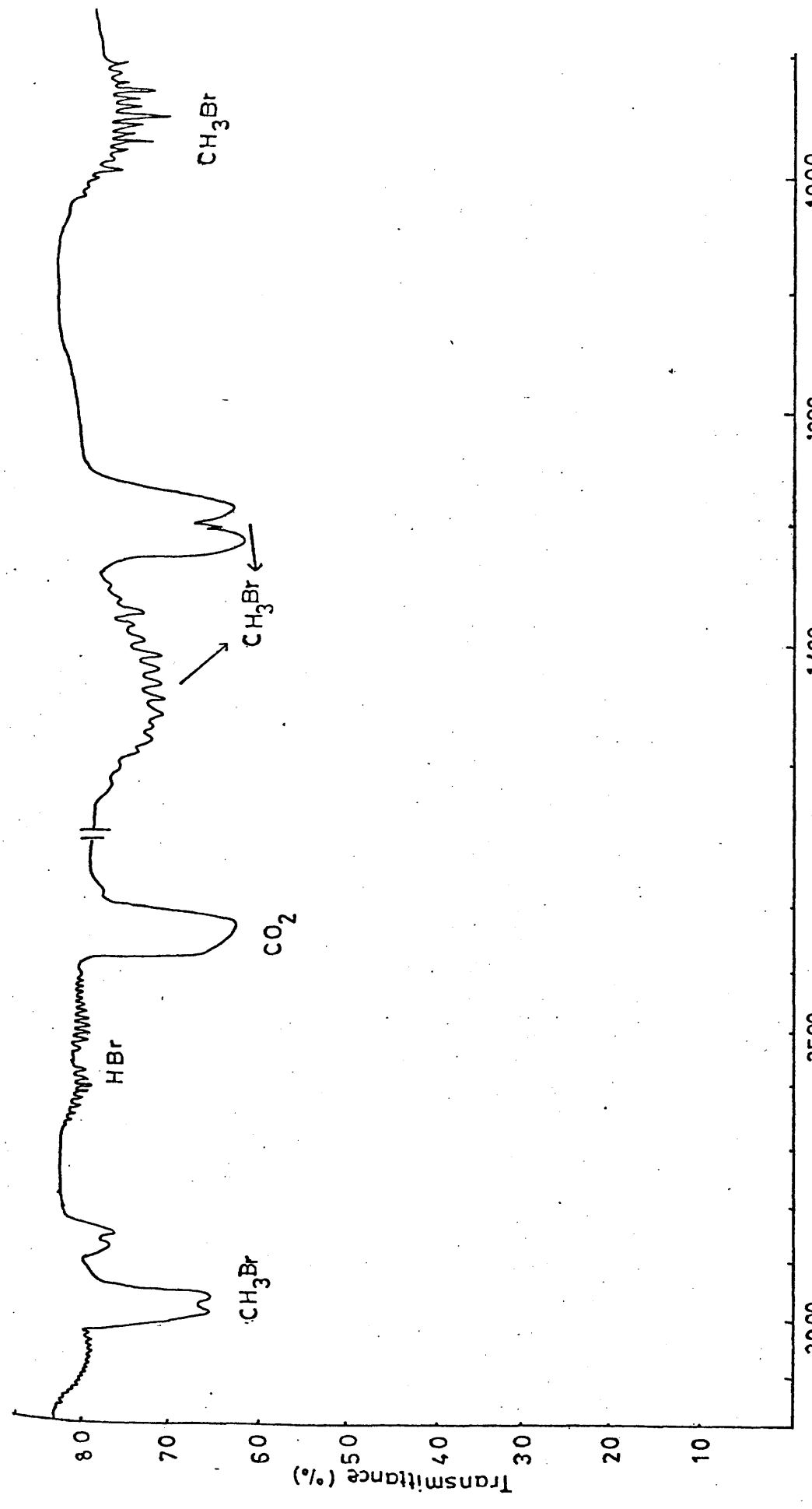


Fig. 5.12. The 900 - 3100 cm^{-1} region of the infra-red spectra of peaks 1 and 2 in the subambient T V A (fig. 5.11).

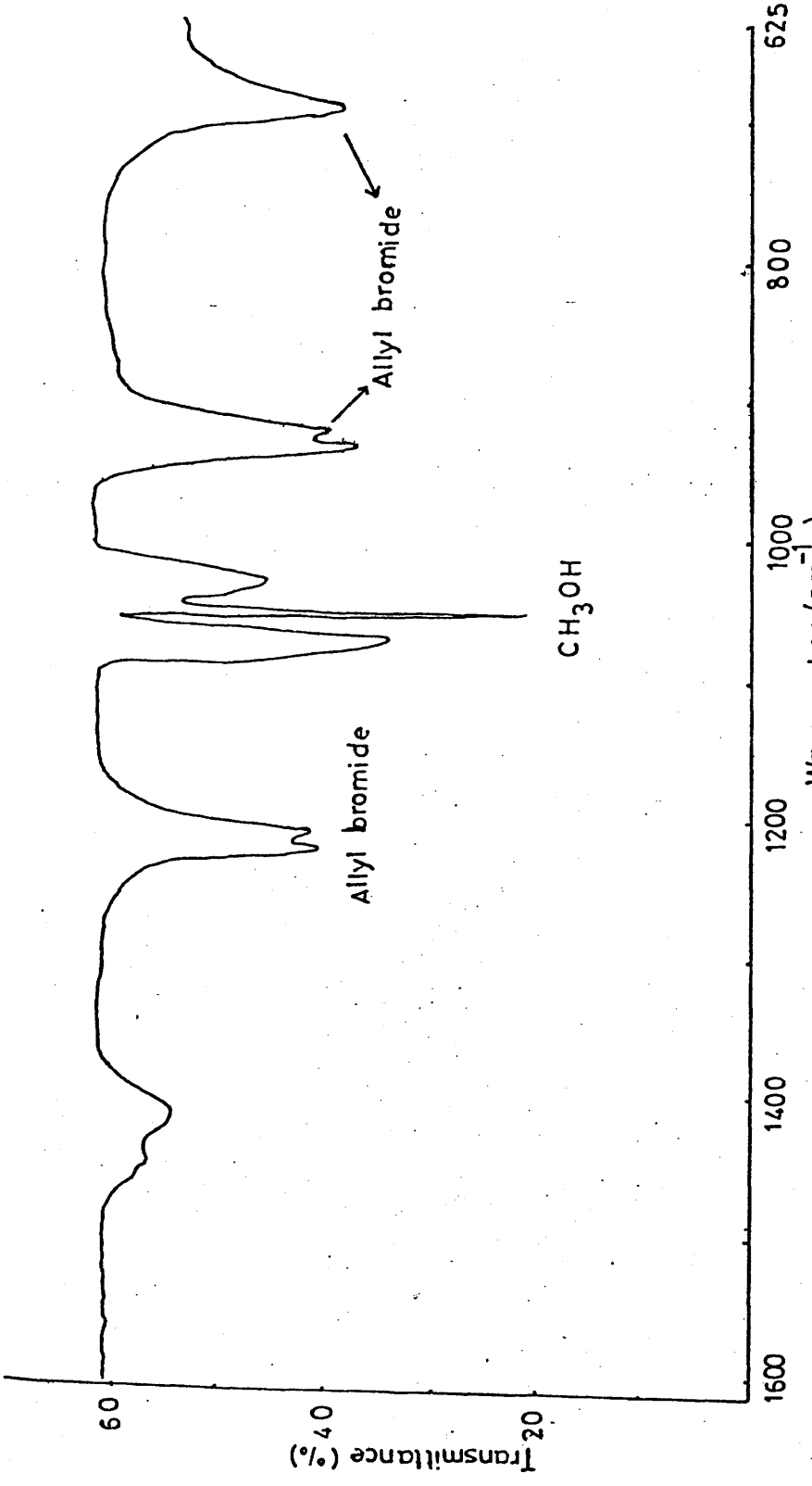


Fig.5.13. The 625 - 1600 cm^{-1} region of the infra-red spectra of peaks 3 and 4 in the subambient T V A curve (fig. 5.11).

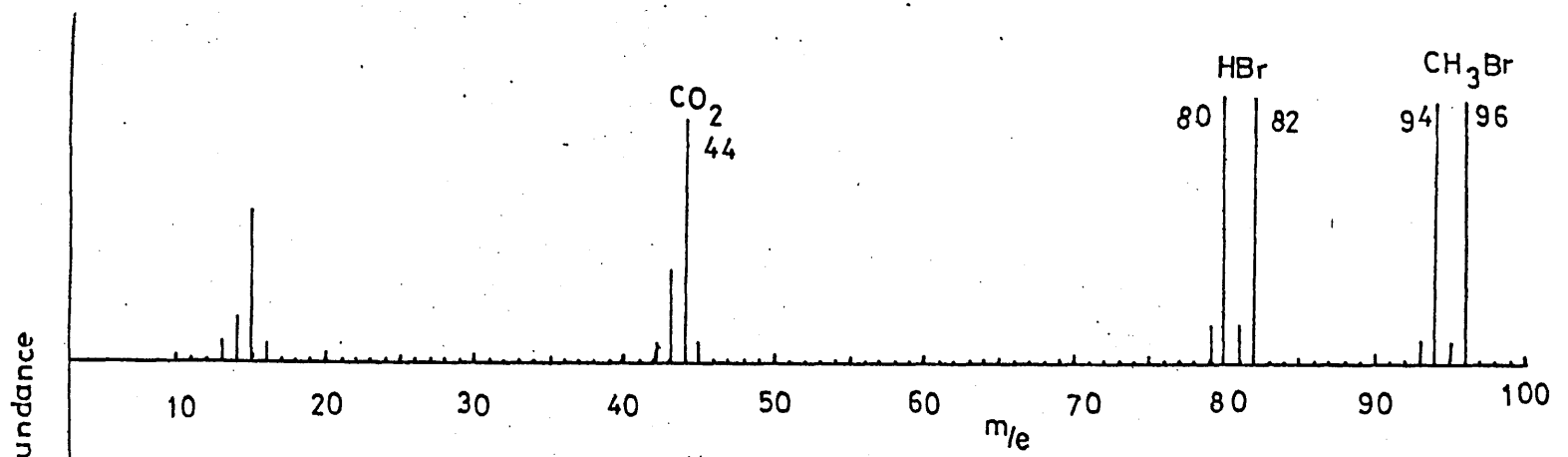


Fig.5.14. Mass spectra of peaks 1 and 2 in the SATVA of 2,3-DBPM-MMA copolymers.

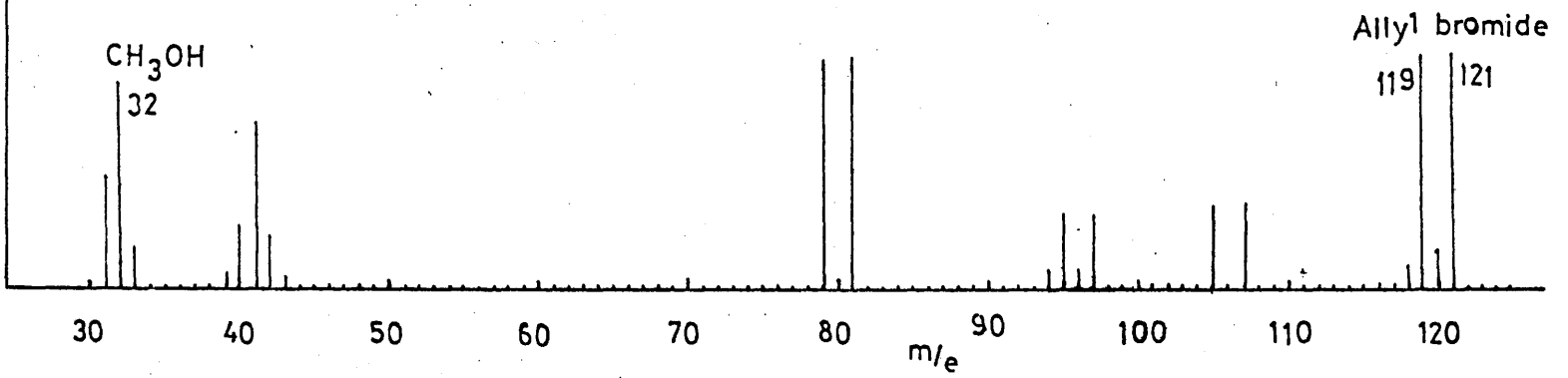


Fig.5.15. Mass spectra of peaks 3 and 4 in the subambient T V A of 2,3 - D B P M - M M A copolymers.

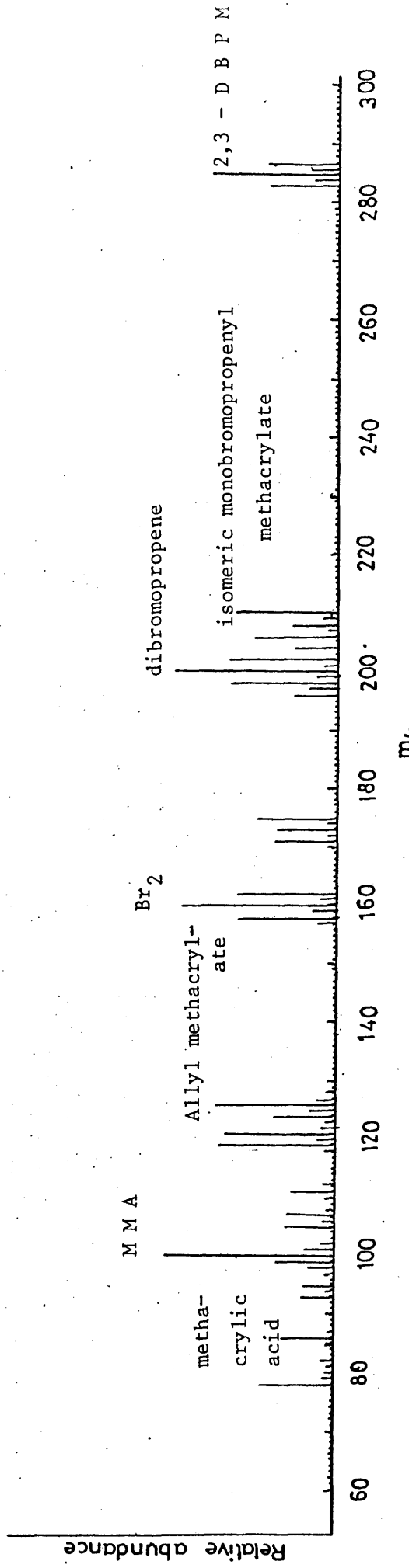


Fig.5.16. Mass spectra of peaks 5, 6 and 7 in the subambient T V A of 2,3 - D B P M - M M A copolymers.

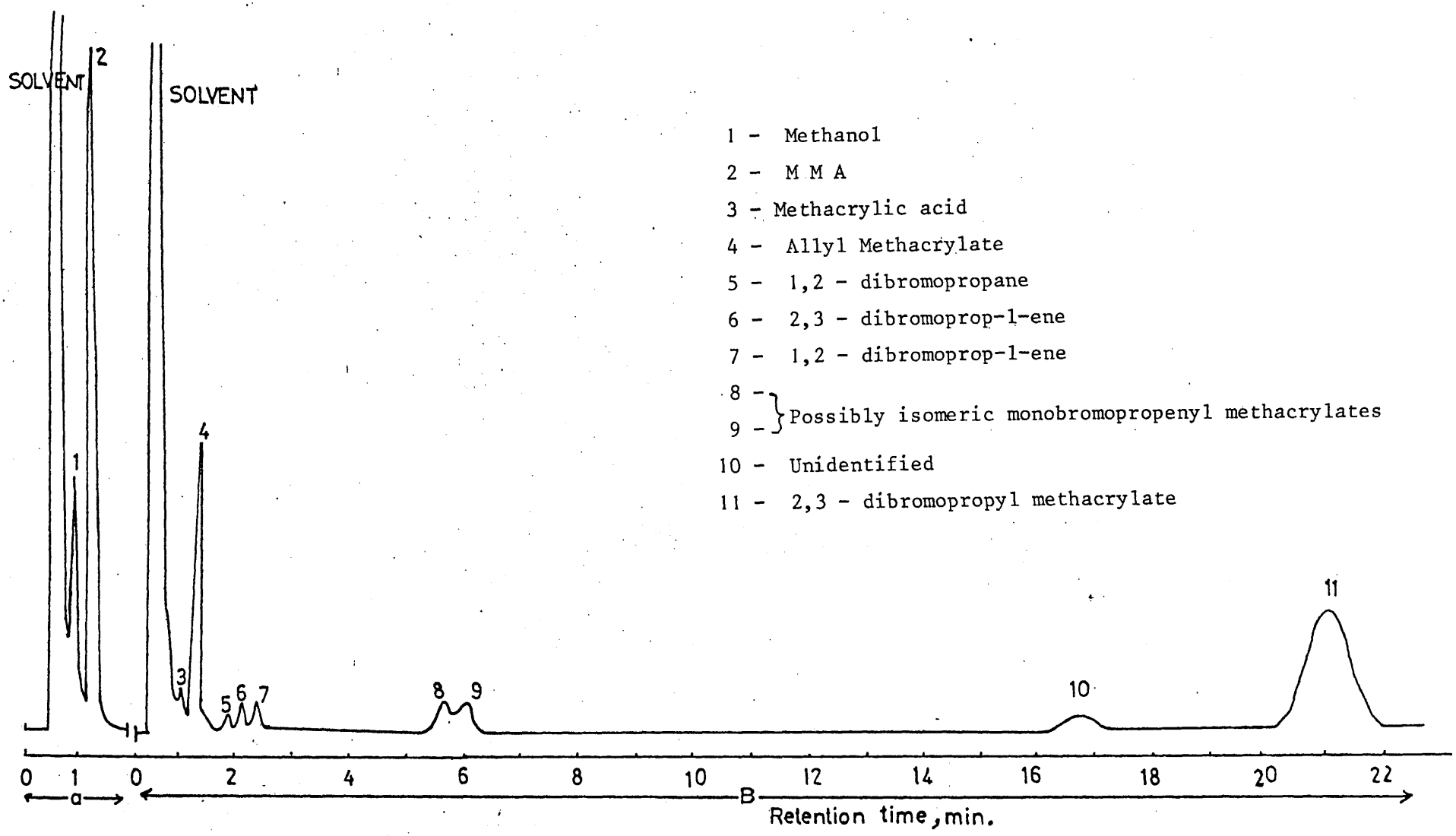


Fig.5.17. G L C trace for the degradation products of peaks 4, 5, 6 and 7 in the subambient T V A curve (fig. 5.11) using 5 ft ¼ inch diameter, 10% microwax on chromosorb column isothermally at a) 90°C b) 140°C.

Table 5.4. (Continued)

Products of Degradation of 2,3 - D B P M - M M A Copolymers

Product fraction	Products	Methods of Analysis
Peak 6 (S A T V A)	Methacrylic acid, allyl methacrylate , 1,2 - dibromopropane , isomeric dibromopropenes, and isomeric monobromo - propenyl methacrylates	mass spectra and g l c
Peak 7 (S A T V A)	2,3 - dibromopropyl methacrylate (monomer)	mass spectra and g l c

The stepwise degradation procedure described in Chapter 4, was carried out on a single sample of A_3 copolymer in the S A T V A apparatus, the temperature of the stages ranging from 200°C to 500°C. The series of S A T V A curves obtained is shown in figure 5.18. The methyl bromide peak (2) first appears at 280°C and reaches a maximum at 300°C, and again at 360°C. The methanol peak (4) appears at 360°C, while peaks 3, 5, 6 and 7 are present at all stages from 200°C. Thus,it seems that methanol first appears in the second stage of degradation. This can be observed by collecting the degradation products for each stage in the S A T V A apparatus (figures 5.19 (a) and 5.19 (b)).

vi. Quantitative Measurement of Degradation Products

Infra-red spectroscopic techniques were used for the quantitative study of the products in peaks 1, 2 and 3, and g l c for the products

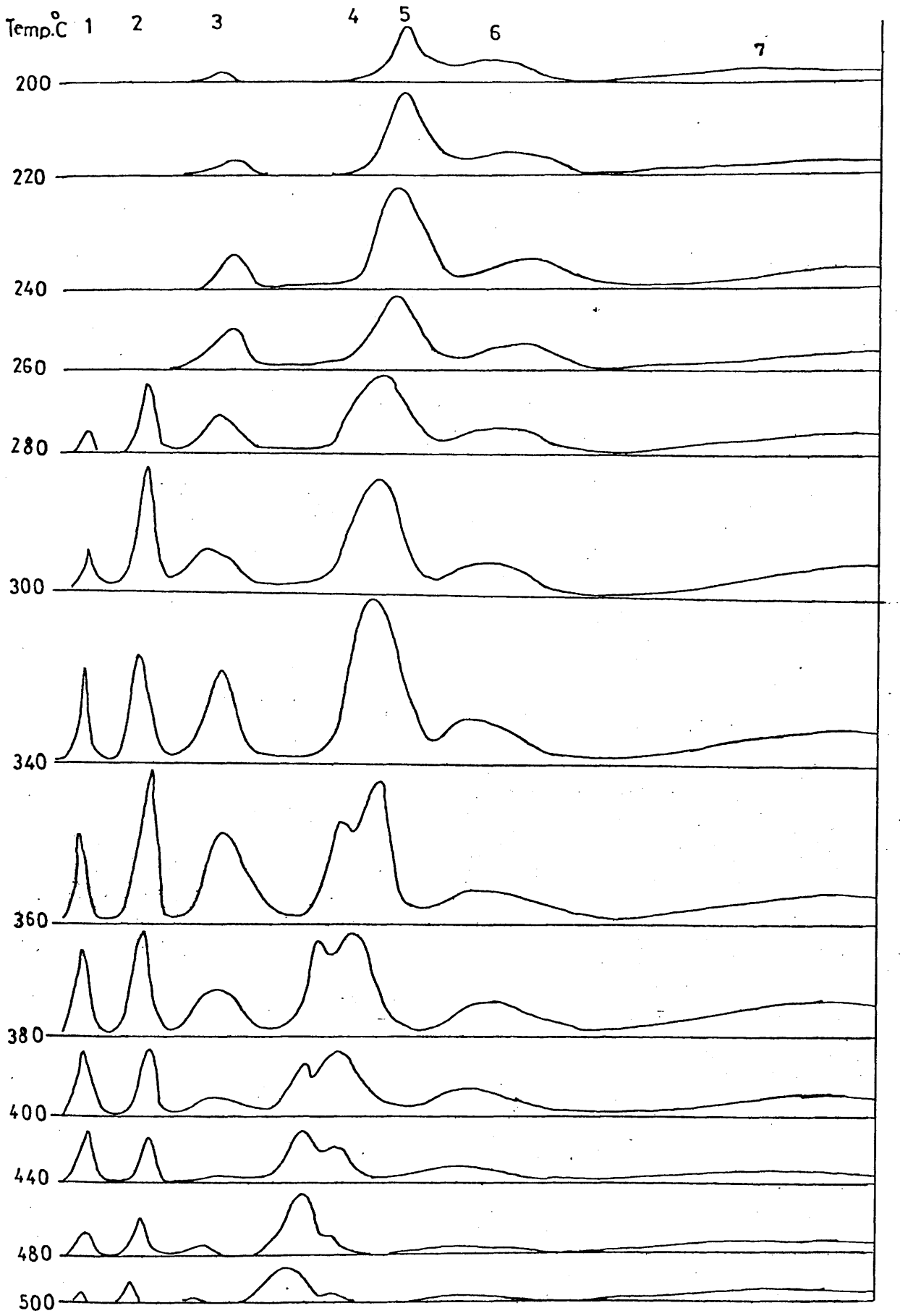


Fig.5.18. Subambient T V A curves for degradation of a single sample of A_3 copolymer (from ambient to successively higher temperature at 10°/min , 50 mg sample size). Sample held at each temperature while products were collected for S A T V A.

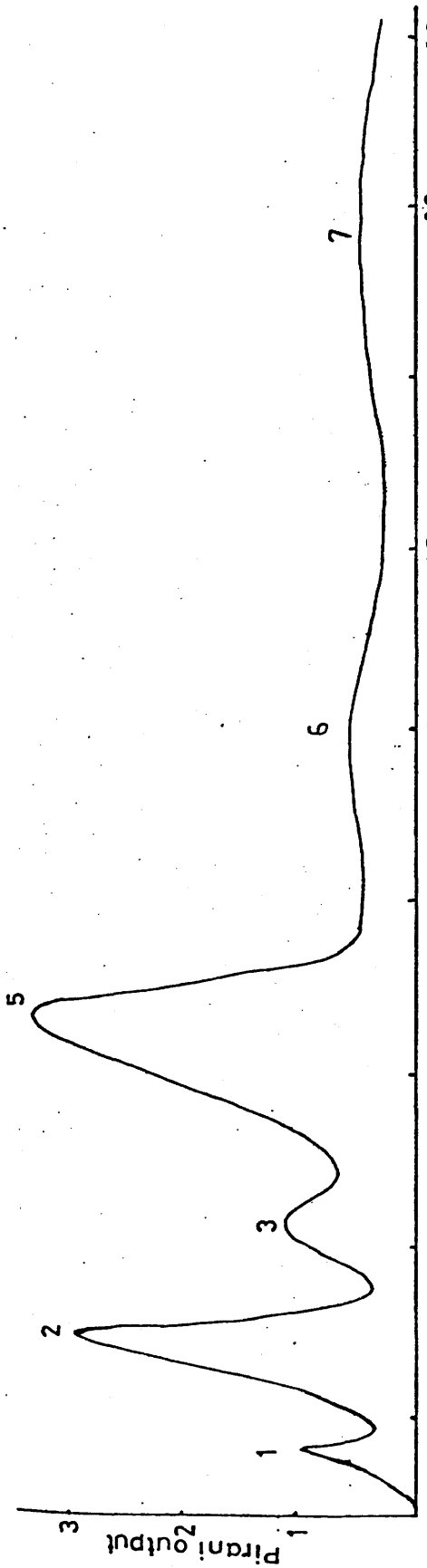


Fig.5.19.(a) Subambient T V A curve for the first stage degradation of A_3 copolymer (from programmed degradation under vacuum at 10^{o}/min , 50 mg sample).

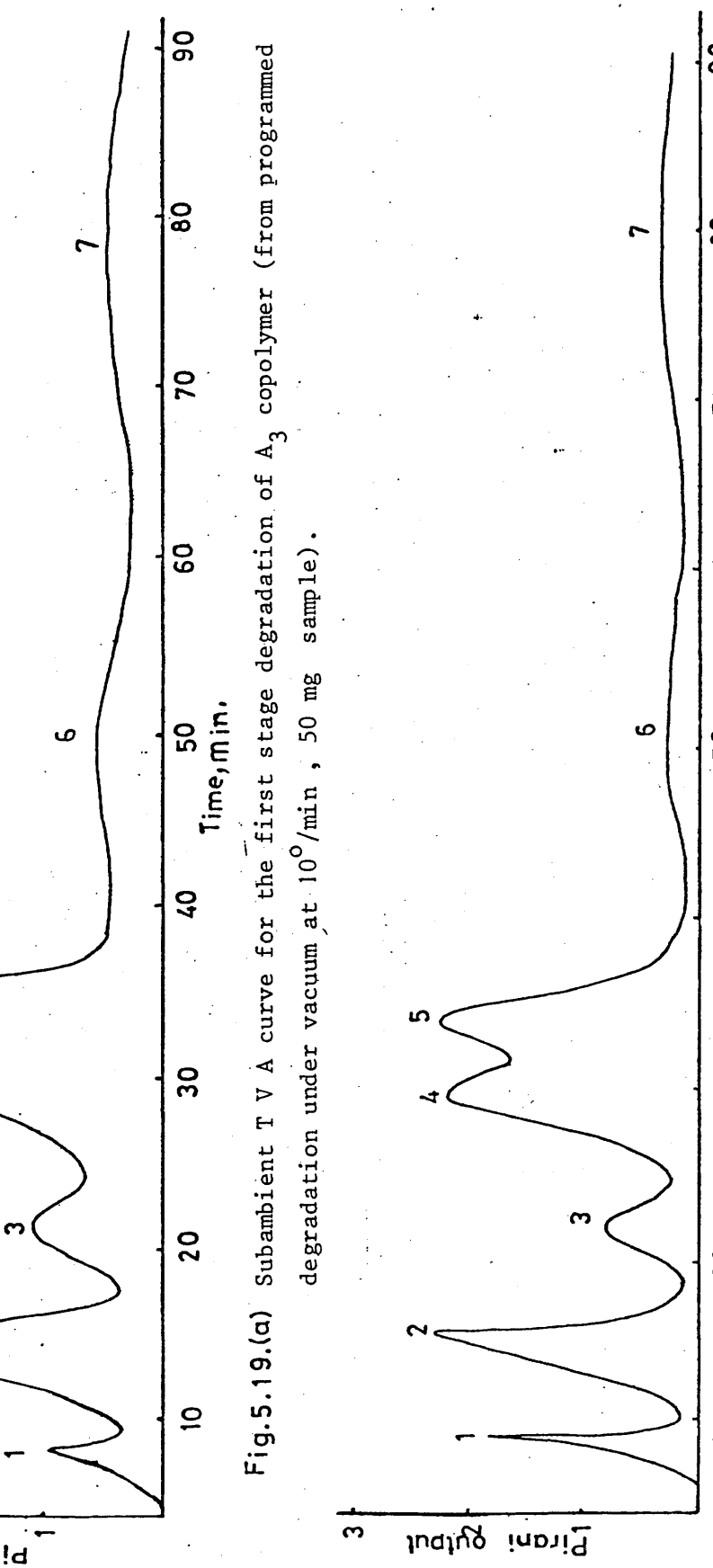


Fig. 5.19. (b) Subambient T V A curve for the second stage degradation of A_3 copolymer (from programmed degradation under vacuum at 10^{o}/min , 50 mg sample).

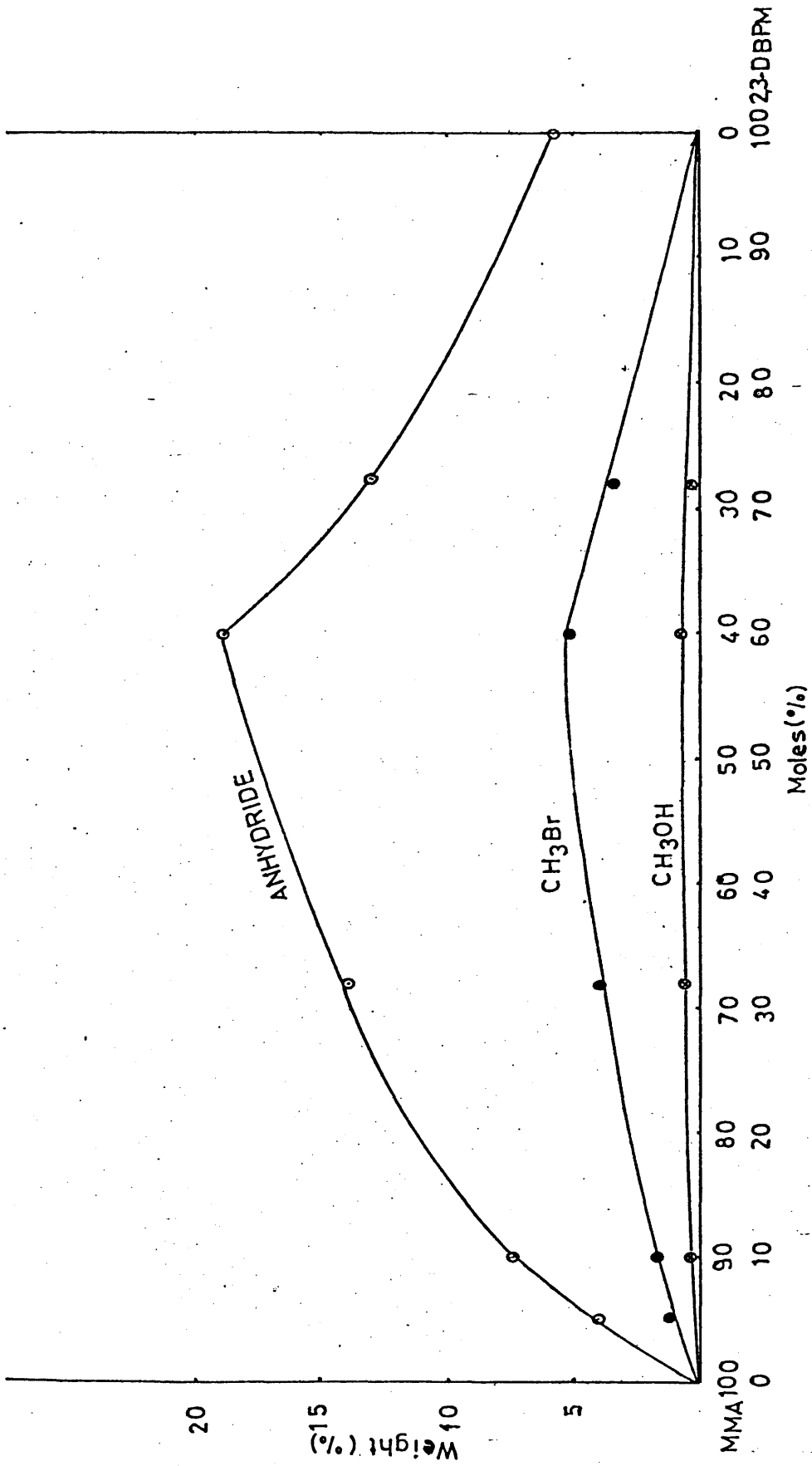


Fig.5.20. CH_3Br , CH_3OH and C R F versus copolymer composition.

in peaks 4, 5, 6 and 7. In the latter case, the product indicated by * in Table 5. 5 is speculative and has not been confirmed by comparison with the pure compound. Figure 5.20 represents the yield of methyl bromide, methanol and anhydride as a function of copolymer composition.

Table 5. 5. Quantitative Analysis of the Products of Degradation of 2,3 - D B P M - M M A Copolymers(20° - 500°C at 10°C/min)

Product	A_1	A_2	A_3	A_4	A_5
			Wt.%		
H Br	3.9	1.9	0.8	trace	trace
CO_2	1.6	1.2	0.9	0.18	0.14
Propene	0.15	0.1	0.1	trace	trace
CH_3Br	3.4	5.1	4.1	1.65	1.2
Allyl bromide	1.7	1.3	1.0	trace	trace
CH_3OH	0.4	0.7	0.5	0.3	trace
MMA (monomer)	19.2	25.1	58.0	80.5	85.80
H_2O	trace	trace	trace	trace	trace
Br_2	2.2	1.8	1.1	0.4	trace
Methacrylic acid	trace	trace	trace	trace	trace
Allyl Methacrylate	1.6	1.1	0.5	0.3	0.2
1,2 - Dibromopropane	0.2	0.1	0.1	trace	trace
Isomeric dibromopropenes	0.4	0.3	0.2	trace	trace
Isomeric monobromopropenyl methacrylates *	1.2	0.6	0.4	0.2	trace
2,3 - D B P M (monomer)	41.3	31.5	14.0	6.1	2.2
C R F (Poly(methacrylic anhydride))	13.5	18.8	14.1	6.9	4
Residue	4	3	3	2	2
Total products identified	94.75	92.6	98.7	98.63	95.54

5. 3 THERMAL DEGRADATION of 2,3 - D B P A - M M A COPOLYMERS

i. Molecular Weights

Five 2,3 - D B P A - M M A copolymers were prepared, as described in Chapter 2, incorporating 56% (A_6) , 42% (A_7) , 18% (A_8) , 14% (A_9) and 9% (A_{10}) of 2,3 - D B P A units. The Number Average Molecular Weights of these copolymers were measured by the method described in Chapter2,and are presented in Table 5. 6. . As the M M A content increases the Number Average Molecular Weights decrease.

Table 5. 6. Number Average Molecular Weights of 2,3 - D B P A - M M A Copolymers

2,3 - D B P M - M M A	Number Average Molecular Weight $\bar{M}_n$
A_6	723,000
A_7	402,000
A_8	327,000
A_9	328,000
A_{10}	264,000

ii. Thermal Volatilisation Analysis (T V A)

T V A thermograms obtained in the degradation of 2,3 - D B P A - M M A copolymers A_6 , A_7 , A_8 , A_9 and A_{10} from ambient temperature to 500°C at 10°C/min are shown in Figures 5.21, 5.22 , 5.23 , 5.24 and 5.25 respectively. There are two distinct peaks, the relative size of each peak being dependant on the copolymer composition. Volatilisation starts in the range 220° - 230°C reaching T_{max} in the first stage between 330° - 340°C and in the region of 380° - 390°C in the second stage. At higher methyl methacrylate contents, the first stage is characterised by significant formation of volatiles condensed in the 0°C trap and traces of volatiles condensed in the -45° , -75° , -100° and -196°C traps. The second stage shows that there are products of a wide range of volatilites and a considerable amount of material is non-condensable at -196°C.
A deep yellow cold ring fraction is formed and may be dissolved in chloroform for infra-red spectroscopic analysis, which shows the existence of chain fragments and methacrylic anhydride groups. A small amount of black residue remains at 500°C.

iii. The Stability of 2,3 - D B P A - M M A Copolymers

Figure 5.26 shows the initial stage of T V A traces of 2,3 - D B P A - M M A copolymers (A_6 , A_7 , A_8 , A_9 and A_{10}) as well as P2,3 - D B P A and P M M A homopolymers. Figure 5.27 shows the effect of copolymer composition on rates of volatilisation at 275°C as measured by the Pirani reading at that temperature. It shows that copolymer A_6 is more stable than any of the other copolymers and even then P2,3 - D B P A and P M M A homopolymers. Since the reactivity ratios of 2,3 - D B P A and M M A are o.38 $\pm$ 0.02 and 1.02 $\pm$ 0.2

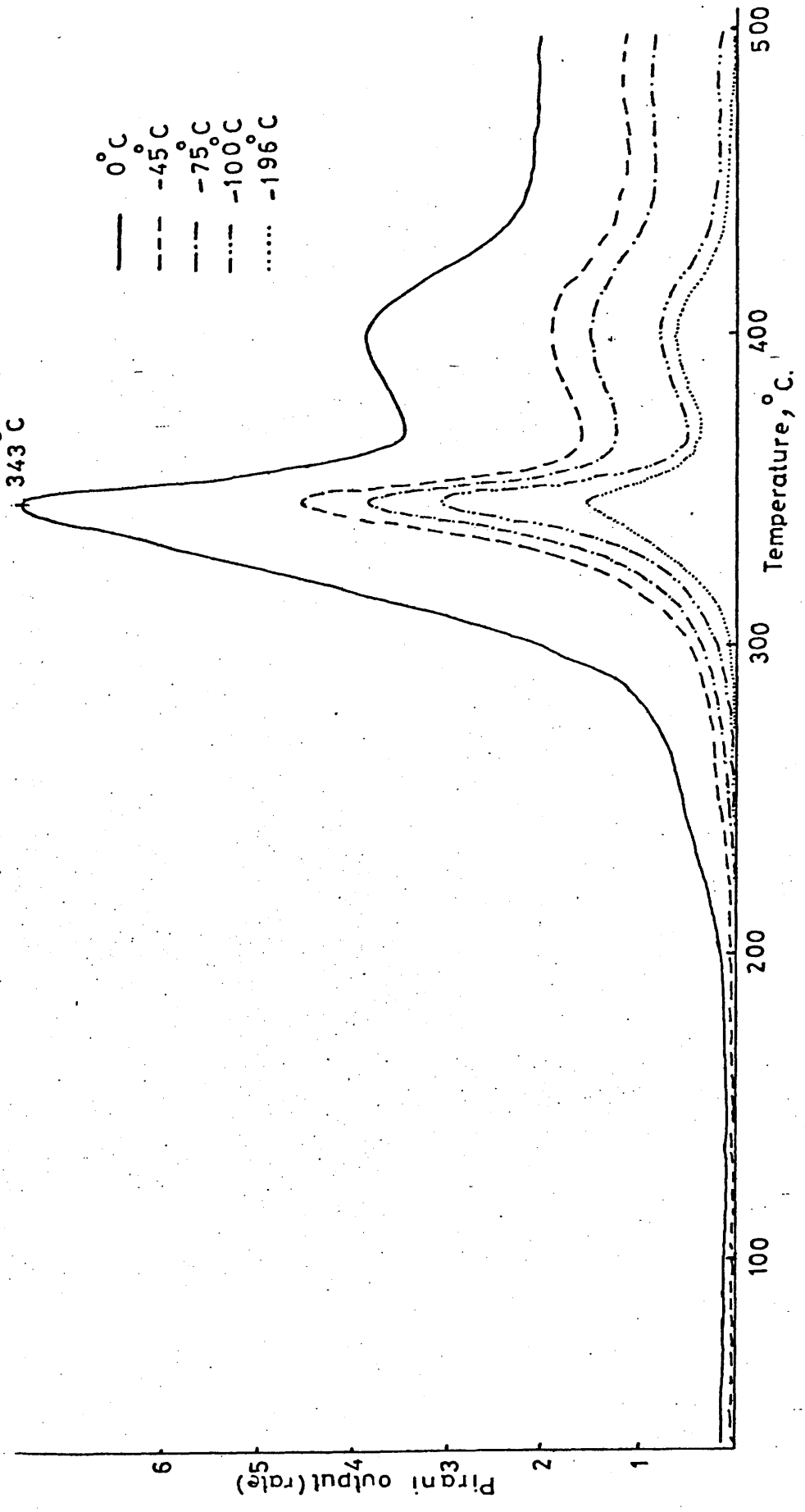


Fig.5.21. T V A curve for A_6 copolymer, sample size 50 mg small pieces; heating rate 10^{o}/min.

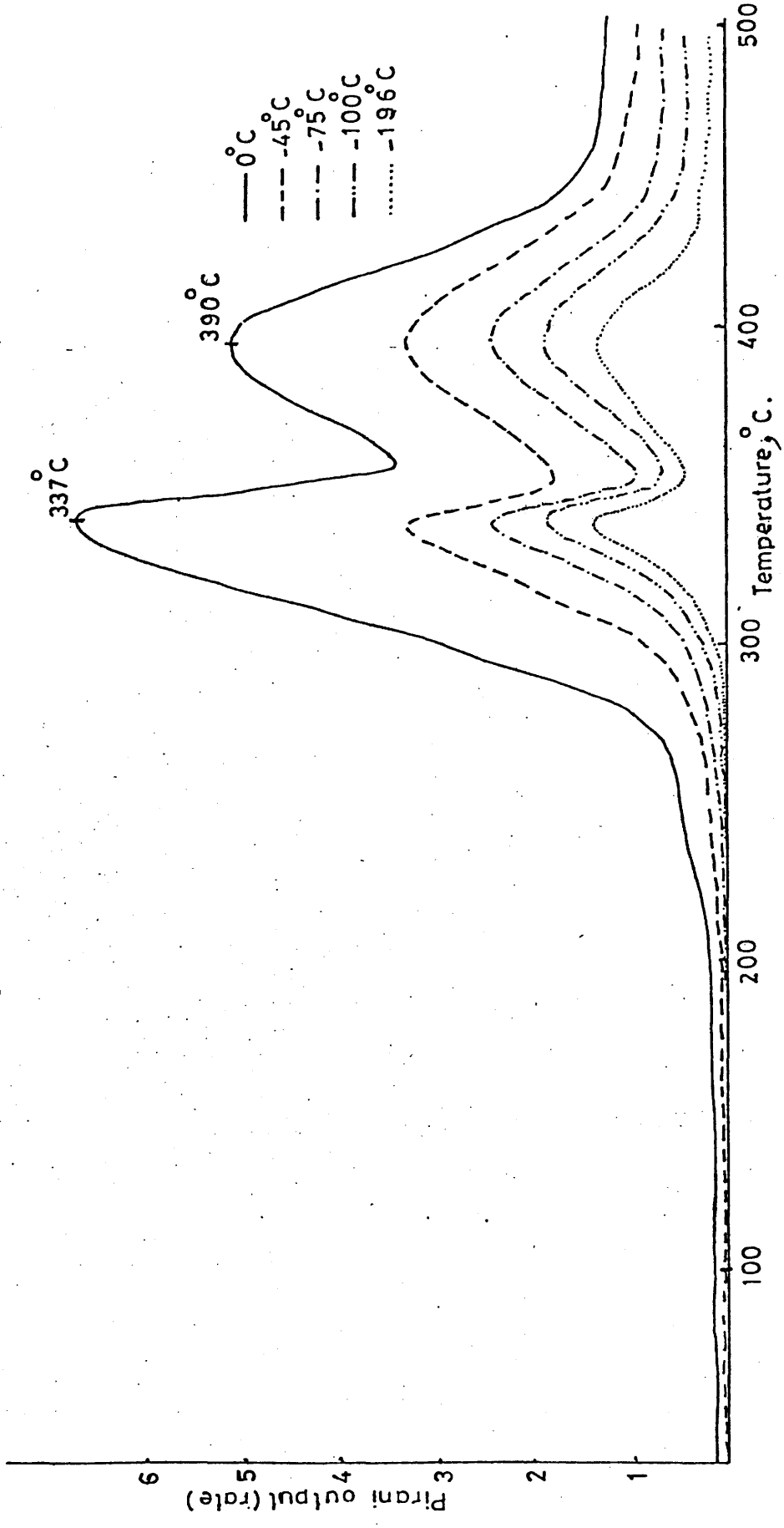


Fig.5.22. T V A curve for A_7 copolymer, sample size 50 mg small pieces; heating rate 10^{o}/min.

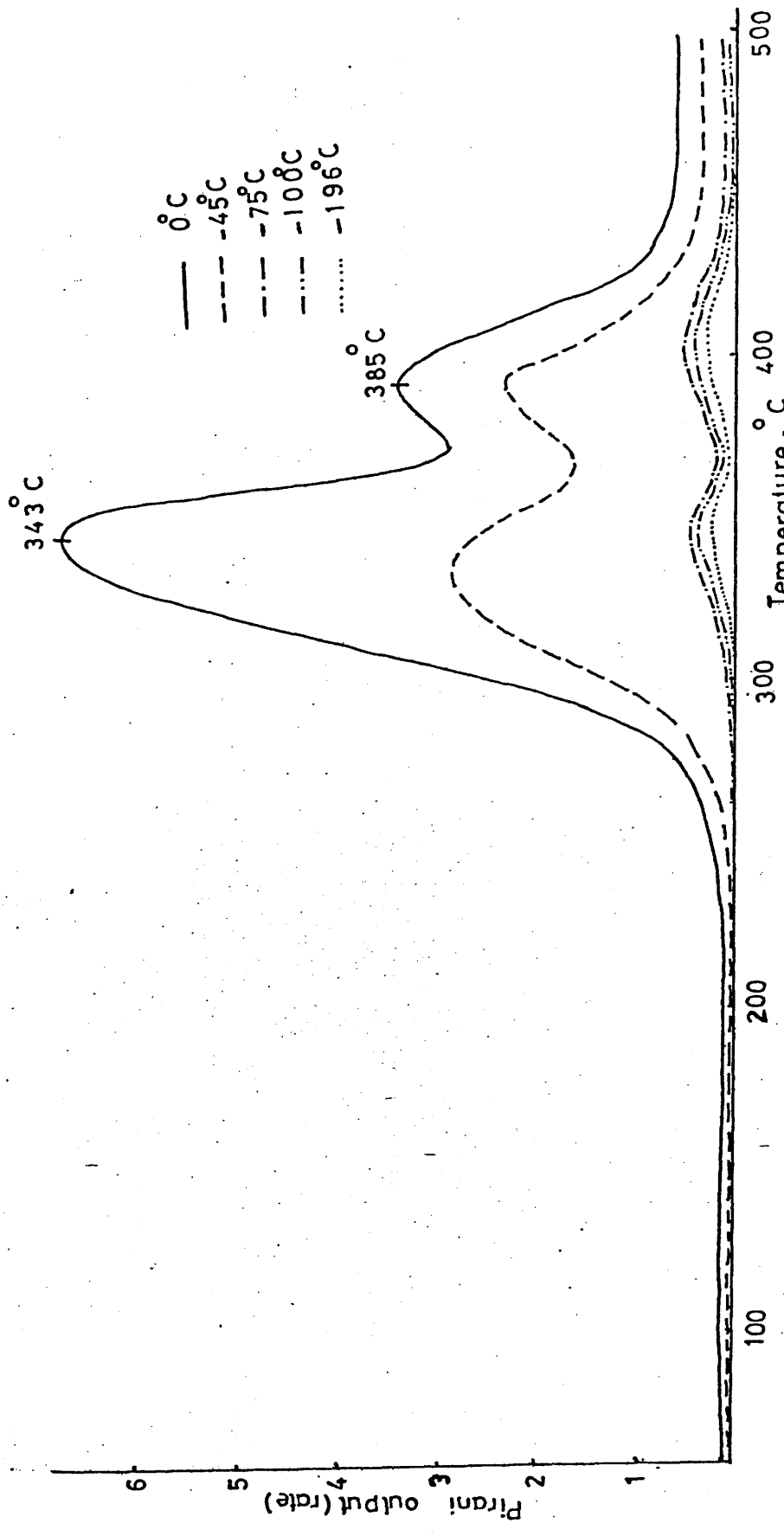


Fig.5.23. T V A curve for A_8 copolymer, sample size 50 mg small pieces; heating rate 10^{o}/min.

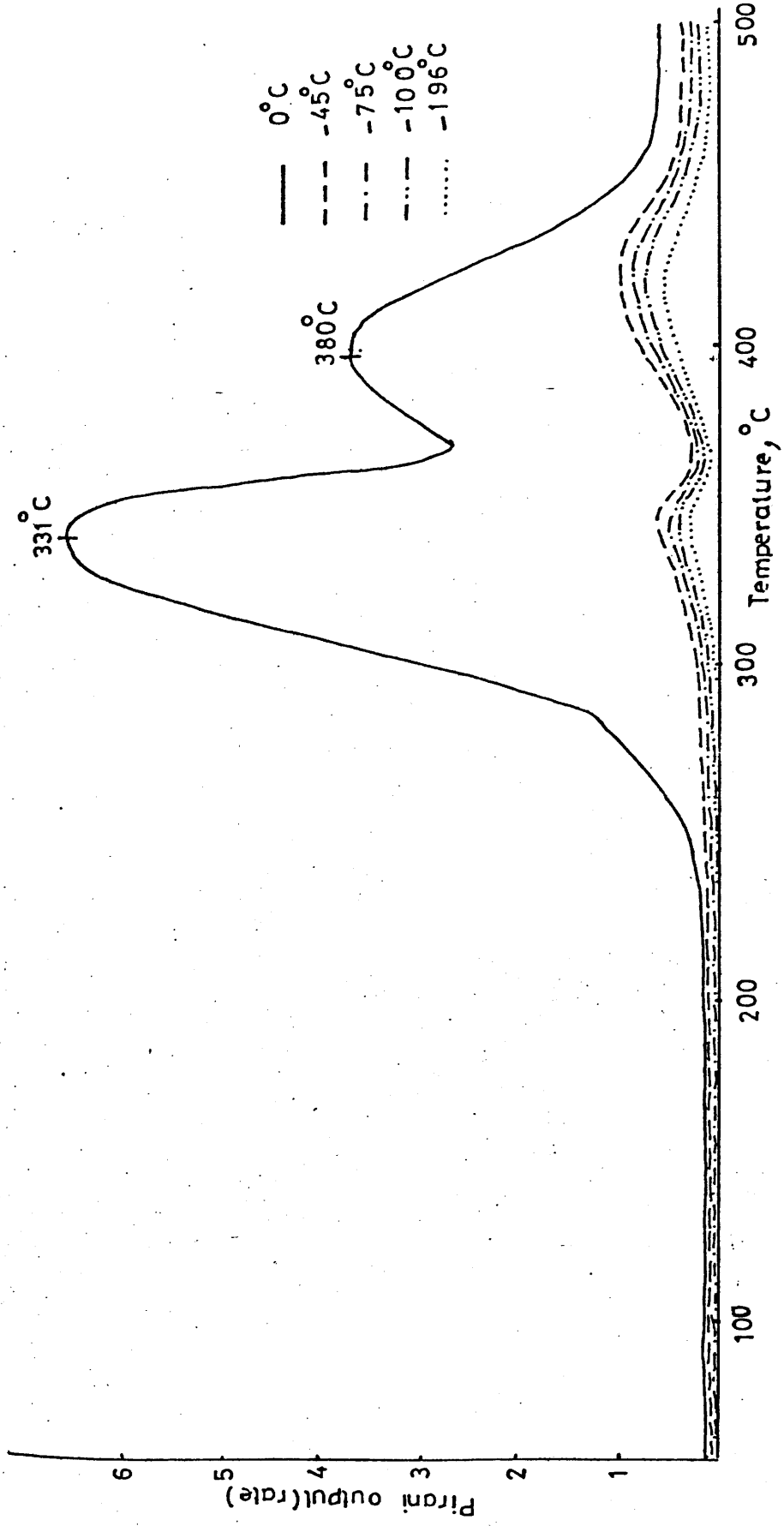


Fig. 5.24, T V A curve for A_9 copolymer, sample size 50 mg ; heating rate 10^{o}/min.

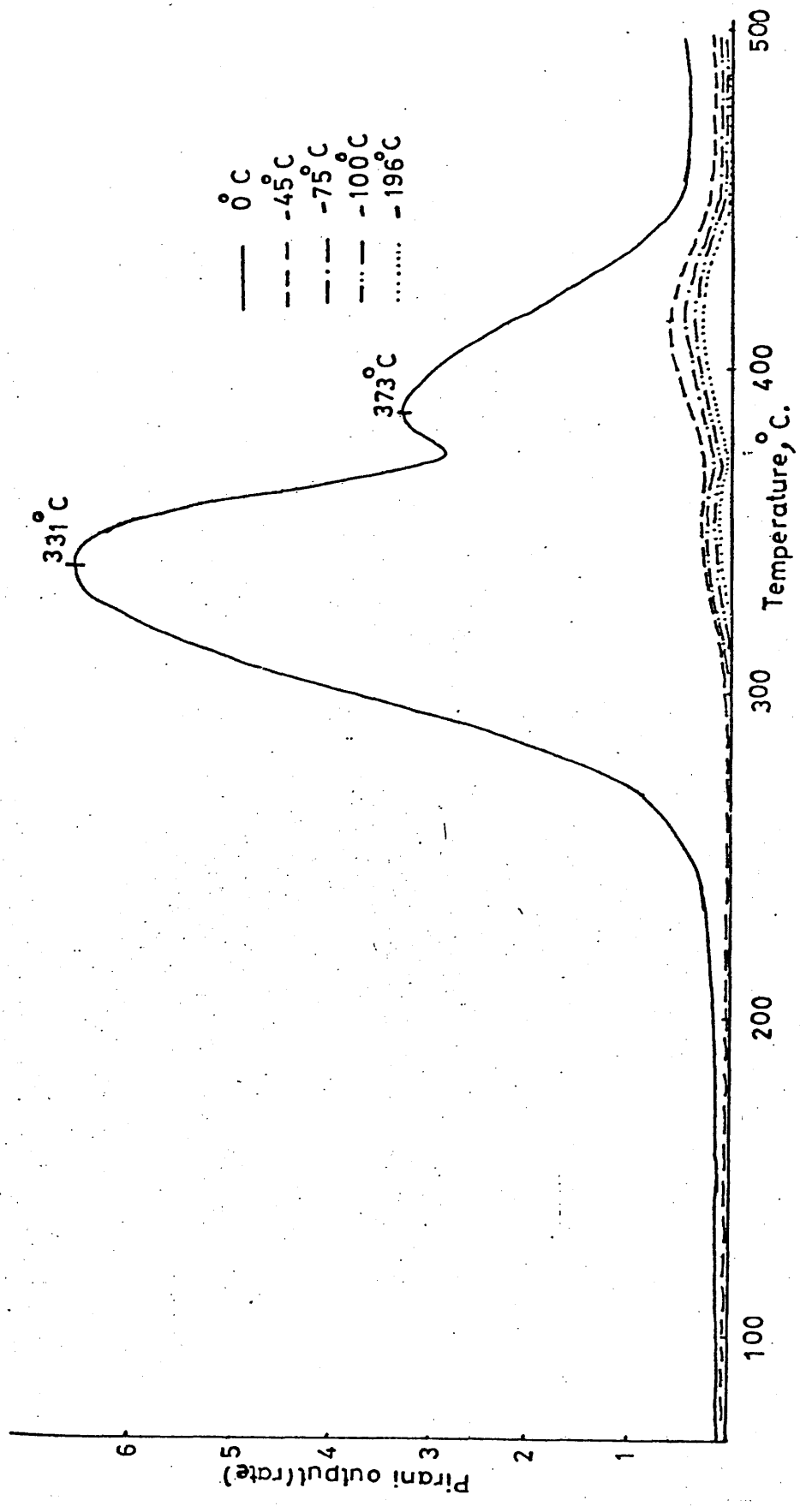


Fig.5.25. T V A curve for A_{10} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

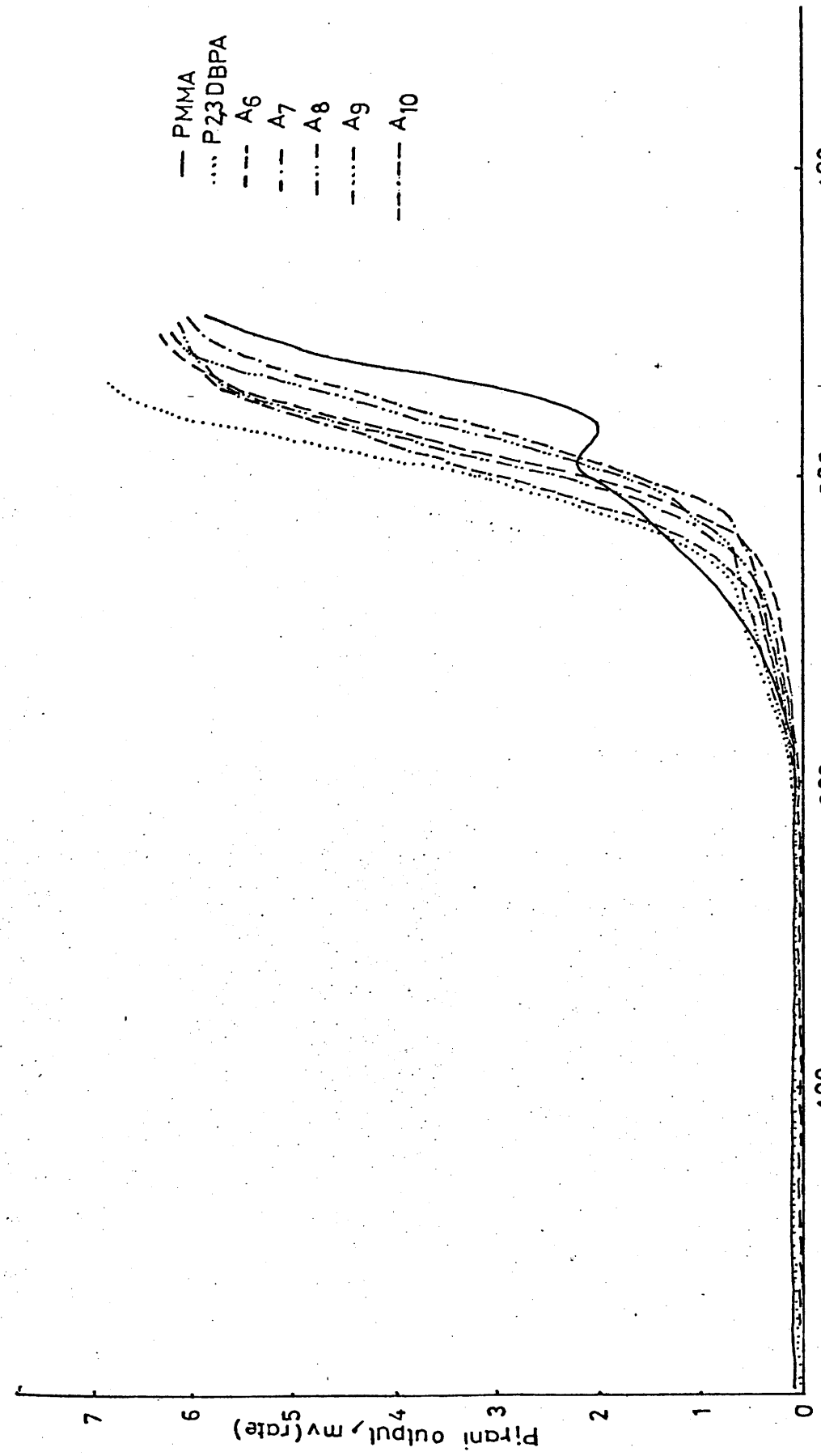


Fig.5.26. Initial stage in T V A thermograms of 2,3 - D B P A - M M A copolymers at 10°/min heating rate, 50 mg sample size.

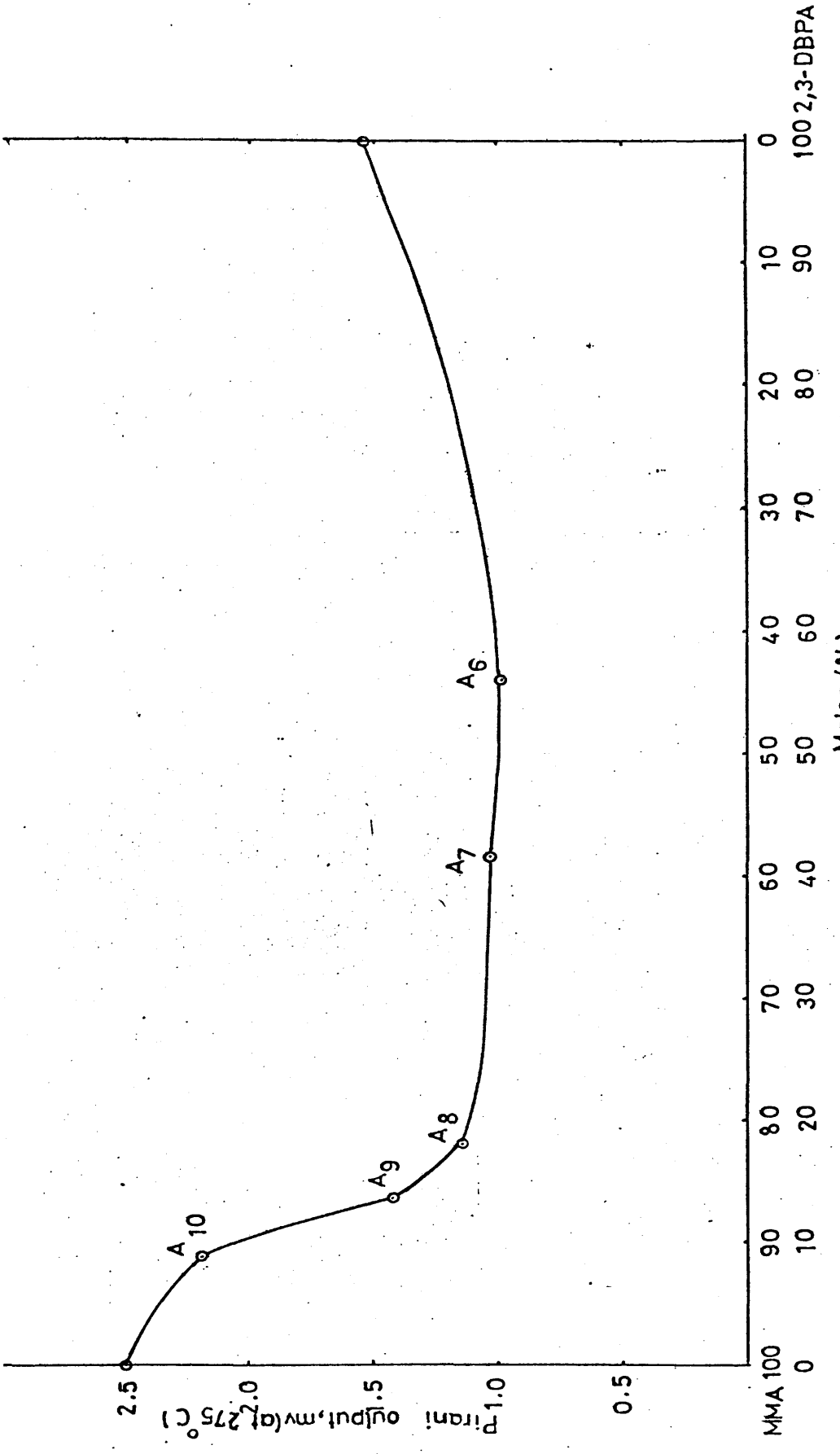


Fig.5.27. Comparison of rate of volatilisation at 270°C as measured by Pirani reading, with copolymer composition, for heating rate 10°/min and sample size 50 mg.

respectively, this suggests that alternating monomer units in the copolymer molecules favour stability

iv. T G and D S C

The weight loss curves for A_6 , A_7 , A_8 , A_9 , A_{10} , P2,3 - D B P A and P M M A are shown in Figure 5.28. Volatilisation starts between 220° - 230°C and degradation occurs in a two stage process as previously shown by T V A. The relative importance of each stage is dependant on the copolymer composition. Table 5. 7 shows the percentage weight losses and the T_{max} values for the homopolymers and copolymers.

Table 5. 7. Weight Loss and T_{max} Values for the Homopolymers and Copolymers.

Polymer	First Stage		First Stage		wt % remaining at 500°C
	T_{max} °C	wt. loss,%	T_{max} °C	wt. loss,%	
P2,3 - D B P A	330	80	420	7	13
A_6	350	70	410	22	8
A_7	360	60	415	32	8
A_8	330	50	395	40	5
A_9	350	67	395	31	2
A_{10}	335	78	380	18	4
P M M A	375	98	-	-	2

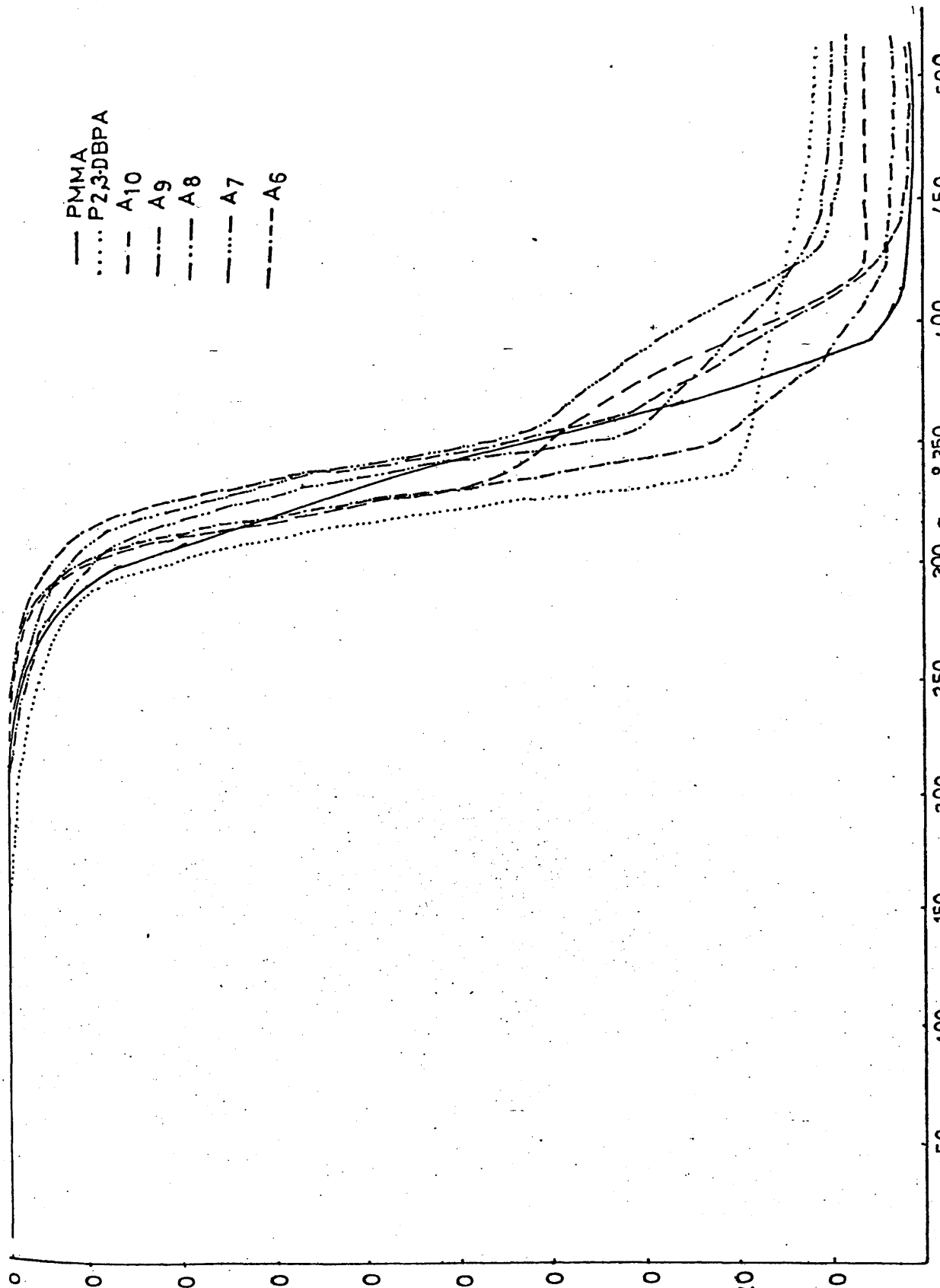


Fig.5.28. T G curves for 2,3 - D B P A - M M A copolymers.

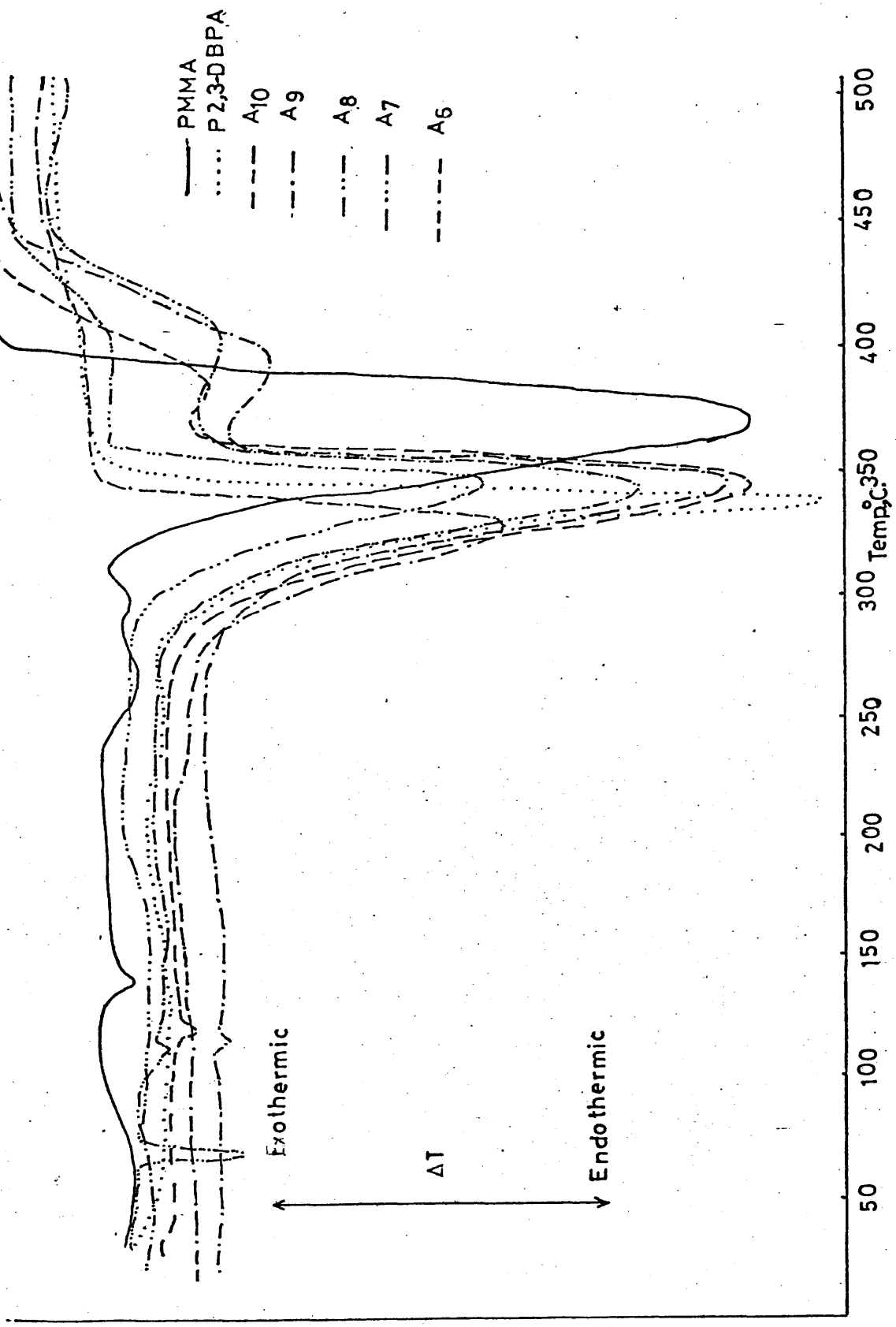


Fig.5.29. D S C curves for 2,3 - D B P A - M M A copolymers.

From figure 5.28 , it is clear that A_6 is more stable than the other copolymers, which is in agreement with the results obtained from T V A.

D S C curves for A_6 , A_7 , A_8 , A_9 , A_{10} , P2,3 - D B P A and P M M A are illustrated in figure 3.29, which shows two endothermic peaks. The glass transition temperature, T_g, of the copolymers are shown in Table 5. 8 It is clear that as 2,3 - D B P A content in the copolymer increases, T_g decreases.

Table 5. 8. T_g for 2,3 - D B P A - M M A copolymers

Polymer	T_g , ^oC
P2,3 - D B P A	-
A_6	50
A_7	65
A_8	110
A_9	112
A_{10}	130
P M M A	135

v. Subambient T V A and Product Analysis

Subambient T V A was carried out using 50 mg of the copolymer samples as described in Chapter 2. Figure 5.30 represents a typical subambient T V A trace, which shows seven peaks and reflects the variety of the products of degradation. The condensable volatile products were examined by infra-red spectroscopy and mass spectra. Non-condensables were also studied by these techniques following degradation of the copolymer in a closed system. The liquid

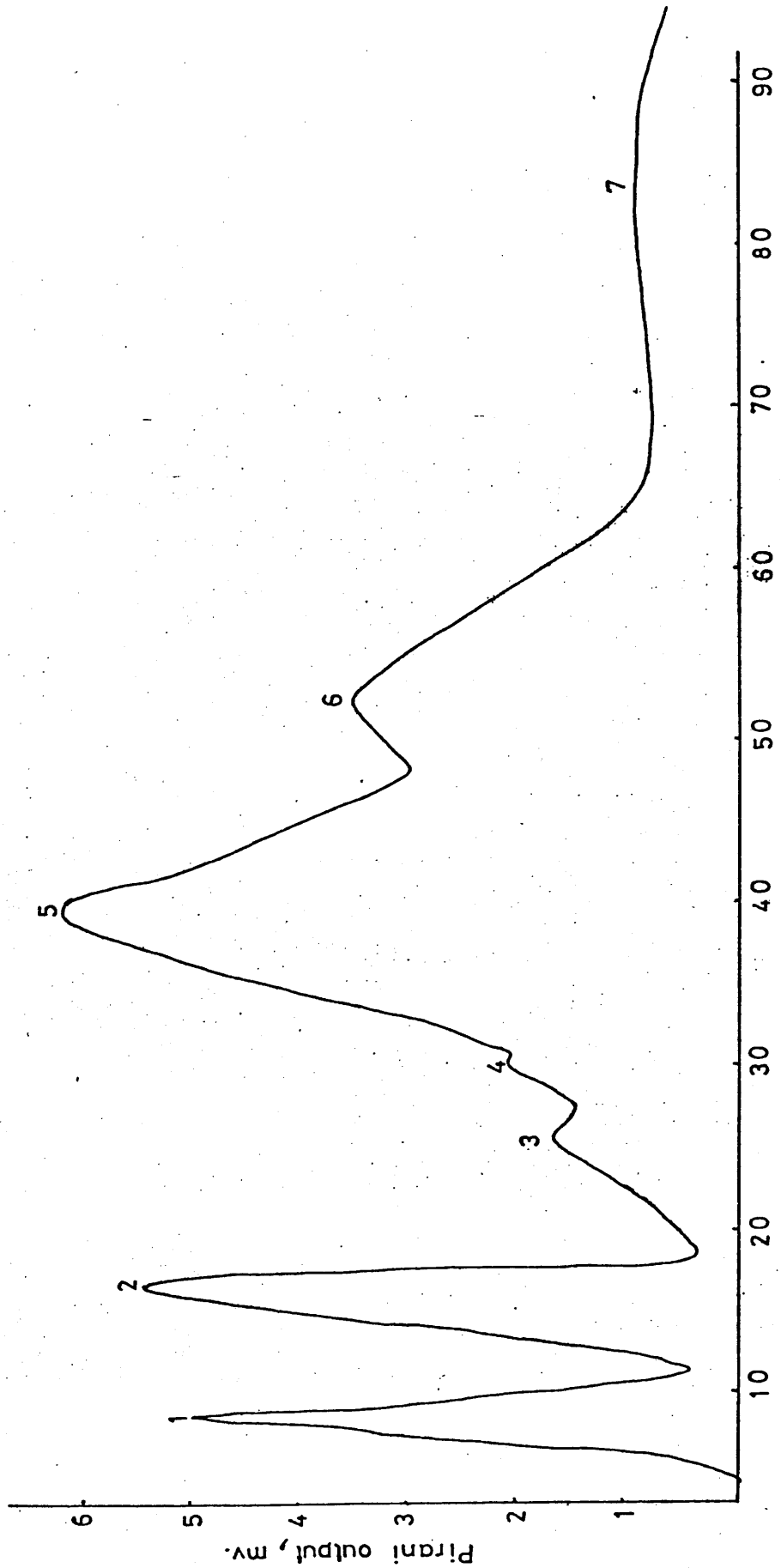


Fig. 5.30. Subambient T V A curve for degradation products of 2,3 - D B P A - M M A (A_8) copolymer (from programmed degradation under vacuum to 500°C at 10°/min , 50 mg sample).

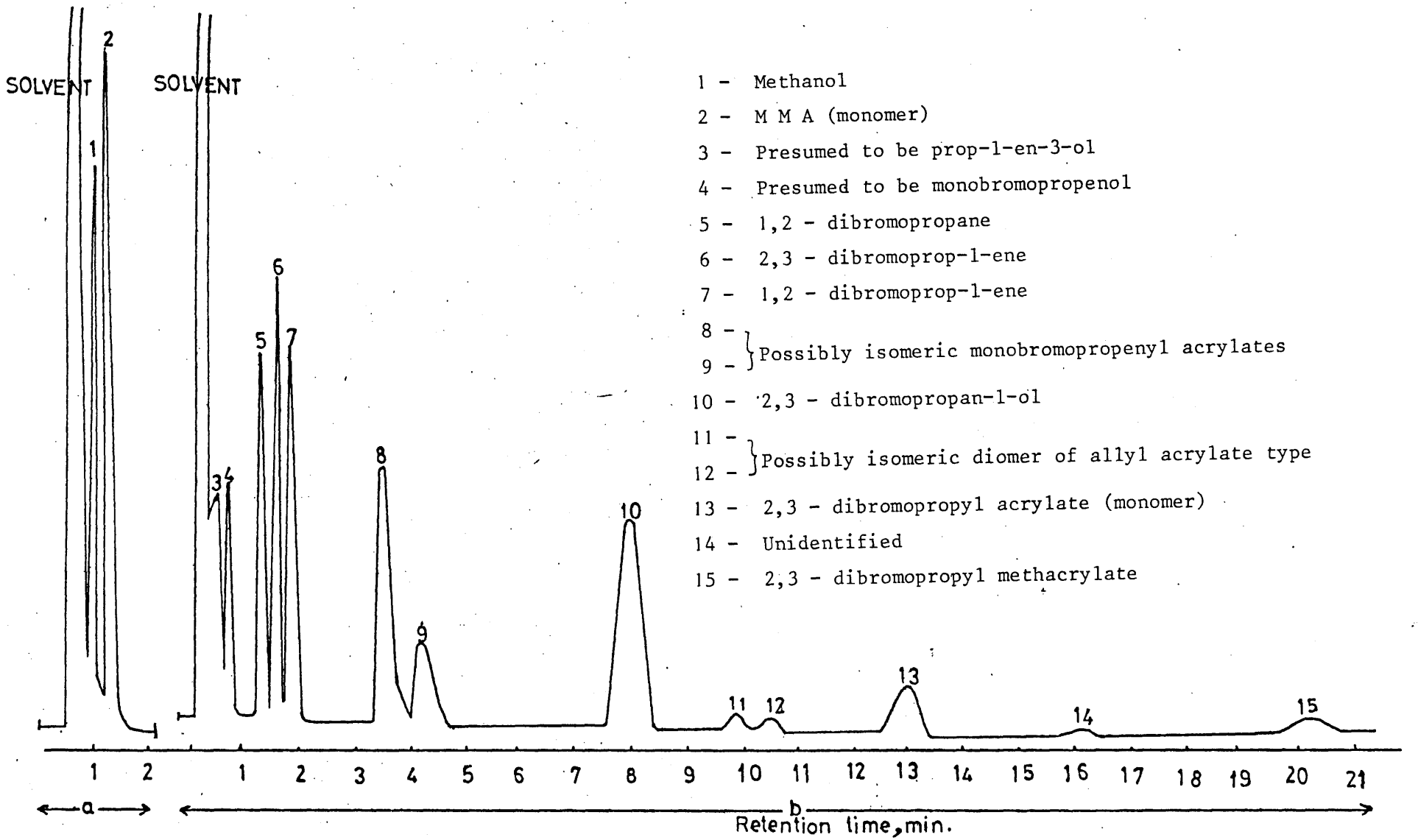


Fig. 5.31. G L C trace for the degradation products of peaks 4, 5, 6 and 7 in the subambient T V A curve (fig. 5.30) using 5 ft. ¼ inch diameter, 10% microwax on chromosorb isothermally at a) 90°C b) 140°C.

products were examined by G L C and mass spectra. Figure 5.31 represents a g l c trace of peaks 4, 5, 6 and 7 of the degradation products from the subambient T V A. A complete list of products of degradation of 2,3 - D B P A - M M A copolymers to 500°C is shown in Table 5. 9.

The products indicated by * could not be confirmed due to the non-availability of reference compounds.

The stepwise degradation procedure, described in Chapter 4 , was carried out on a single sample of A_8 copolymer using the subambient apparatus. The series of S A T V A curves obtained is shown in figure 5.32. Methyl bromide peaks appear at 280°C showing a maximum at 300°C and another maximum at 360°C, as in the 2,3 - D B P M - M M A copolymer degradation. The methanol peak appears at 360°C suggesting that it is produced only in the second stage of the degradation. Peaks 5, 6 and 7 are present at all stages from 230°C.

vi. Quantitative Estimation of the Degradation Products

Table 5. 10 records a quantitative study of the products of degradation of 2,3 - D B P A - M M A copolymers. I r spectroscopic techniques were used for the analysis of the products of peaks 1, 2 and 3 and g l c techniques for the products in peaks 4, 5, 6 and 7. Again materials marked * have not been confirmed. Figure 5.33 shows the variation of CH_3Br, CH_3OH and C R F formation with the copolymer composition.

Table 5. 9. Products of Degradation of 2,3 D B P A - M M A Copolymers

Fractions	Products	Methods of Analysis
Non-condensable	Hydrogen, CO , methane and propene	i r and mass spectra
Cold ring fraction	Chain fragment and polymethacrylic anhydride	i r in solution
Residue	Carbon	i r (K Br disc)
Peak 1 in the S A T V A	HBr , CO_2	i r and mass spectra
Peak 2 in the S A T V A	CH_3Br	i r and mass spectra
Peak 3 in the S A T V A	Allyl bromide	i r and mass spectra
Peak 4 in the S A T V A	Methanol	i r , mass spectra and g l c
Peak 5 in the S A T V A	M M A and H_2O	mass spectra and g l c
Peak 6 in the S A T V A	Methacrylic acid, prop-1-en-3-ol*, monobromo-propenol* , 1, 2 - dibromopropane, 2, 3 - dibromoprop-1-ene, 1, 2 - dibromo-prop-1-ene, Isomeric monobromopropenyl acry-lates *	mass spectra and g l c
Peak 7 in the S A T V A	2,3 - dibromopropan-1-ol, Isomeric dimeric species based on allyl acrylate*, 2,3 - D B P A (monomer) and 2,3 - dibromopropyl methacrylate.	mass spectra and g l c

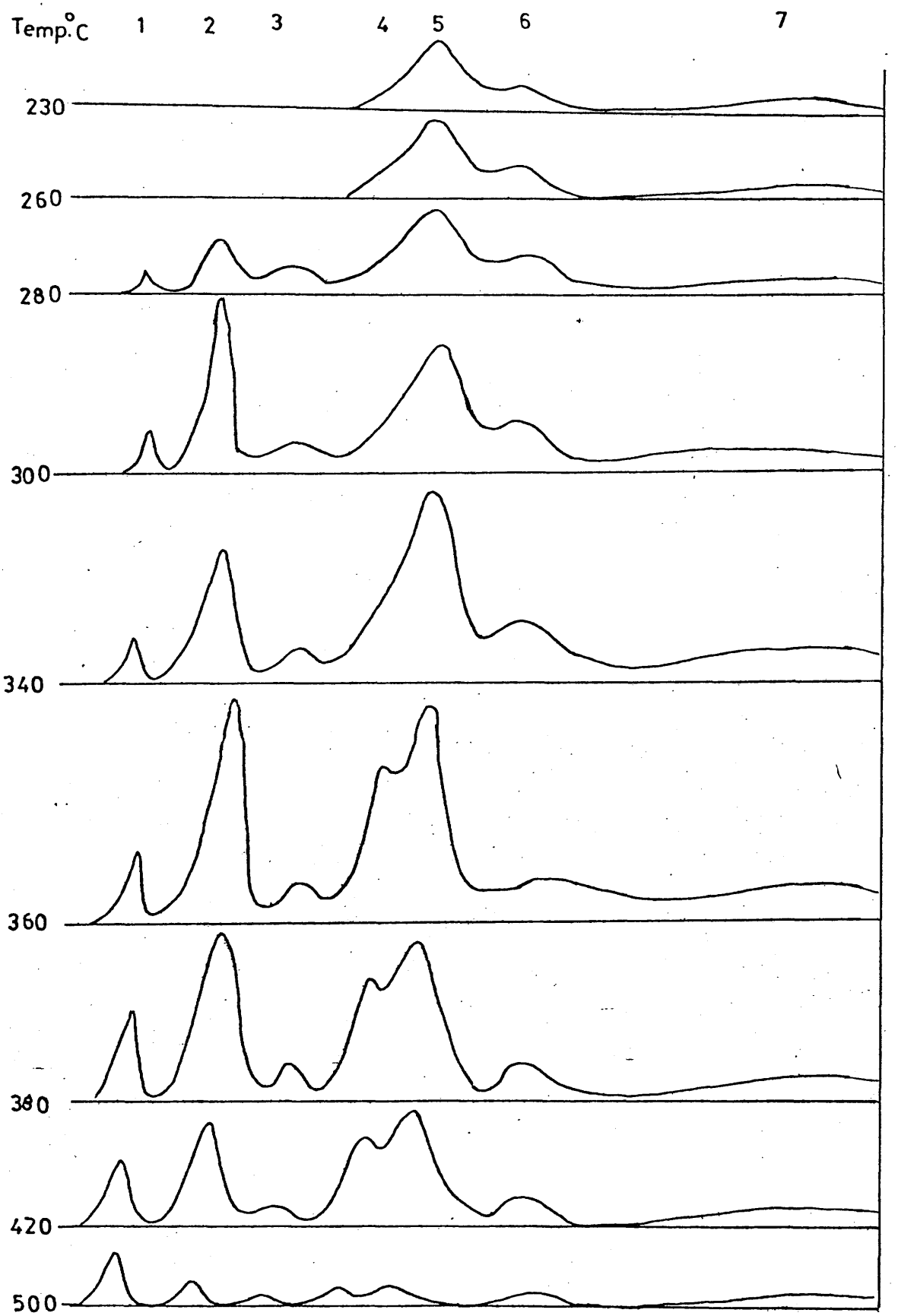


Fig. 5.32. Subambient T V A curves for degradation of a single sample of A_8 copolymer (from ambient to successively higher temperature at 10°/min , 50 mg sample size). Sample held at each temperature while products were collected for S A T V A.

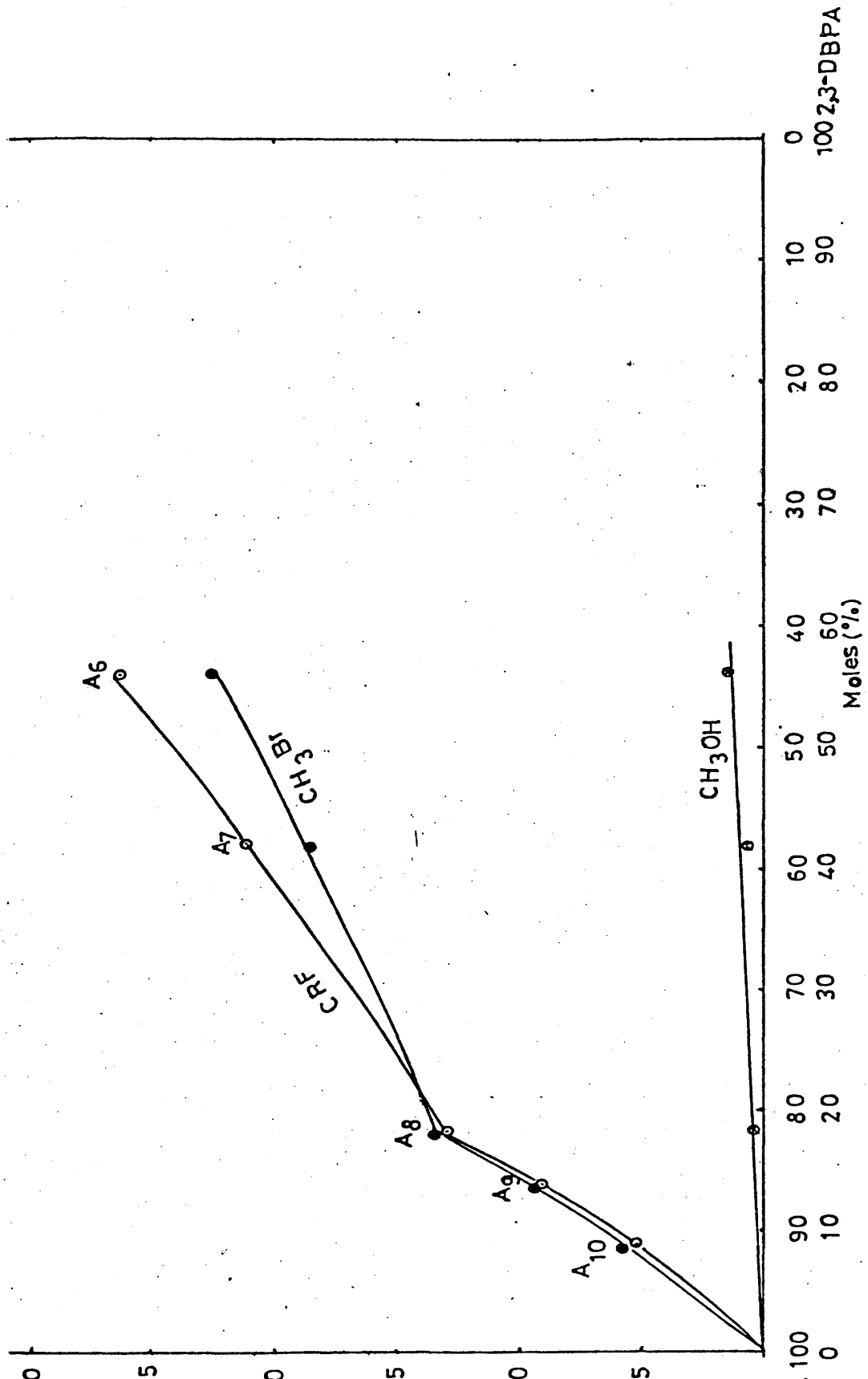


Fig. 5.33. CH_3Br, CH_3OH and C R F versus the copolymer composition.

Table 5.10. Quantitative Analysis of the products of degradation of 2,3 - D B P A - M M A copolymers (20^{o}-500^{o}C, at 10^{o}/min)

Product	A_6	A_7	A_8	A_9	A_{10}
			Wt.%		
H Br	4.20	2.5	1.00	trace	trace
CO_2	4.61	3.16	1.4	1.1	0.70
Propene	0.4	0.3	0.2	-	-
CH_3Br	22.37	18.33	13.04	8.04	5.89
Allyl bromide	4.63	3.17	1.42	1.22	0.76
CH_3OH	1.5	0.83	0.62	trace	trace
M M A (monomer)	18.2	37.1	58.3	74.2	80.7
H_2O	trace	trace	trace	trace	trace
Methacrylic acid	trace	trace	trace	trace	trace
Prop-1-en-3-ol *	0.4	0.3	0.1	trace	trace
Monobromoprop-1-en-3-ol *	0.4	0.3	0.1	trace	trace
1,2 - dibromopropane	1.5	1.0	0.5	0.3	0.2
2,3 - dibromoprop-1-ene	2.3	1.5	0.7	0.4	0.3
1,2 - dibromoprop-1-ene	1.9	1.2	0.6	0.4	0.3
Isomeric monobromopropenyl acrylates *	3.0	1.9	0.7	0.3	0.2
2,3 - dibromopropan-1-ol	2.2	1.9	1.0	0.6	0.5
Isomeric dimeric species based on allyl acrylate *	1.0	0.7	0.8	0.7	0.7
2,3 - dibromopropyl acrylate (monomer)	0.9	1.3	1.6	1.9	2.2
2,3 - dibromopropyl methacrylate	trace	trace	trace	trace	trace
C R F (chain fragments + poly (methacrylic anhydride))	27.5	21.31	13.2	8.0	5.2
Residue	2	2	2	2	2
Total product	99.01	98.8	97.28	99.16	99.65

5.3 DISCUSSION

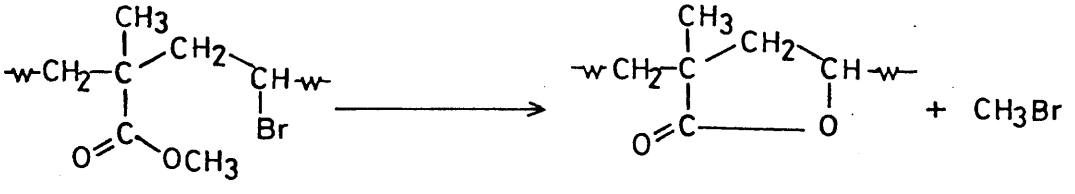
The formation of methyl bromide and methanol, neither of which are formedin the decomposition of either of the homopolymers, demonstrates that interaction takes place between both thebrominated monomers and M M A during decomposition of the copolymers. But perhaps the most surprising result is the tremendous decrease in the proportion of HBr, especially in the degradation of 2,3 - D B P A - M M A copolymers. The other degradation products formed in the degradation of P 2,3 - D B P M and P 2,3 - D B P A homopolymers were observed also in the degradation of the corresponding copolymers, although gradually decreasing in amount as the proportion of M M A in the copolymer is increased. In discussing the detailed reaction mechanisms of these copolymer systems, it is convenient to consider the two copolymers separately.

i. 2,3 - D B P M - M M A Copolymer

a. The predominating degradation products are the two monomers, M M A varying from 19.2% to 85.8% and 2,3 - D B P M from 41% to2.2% as shown in Table 5.5. The formation of these monomers reflects the characteristic mode of polymethacrylate degradation observed by Grassie[19] and described earlier in Chapter 4.

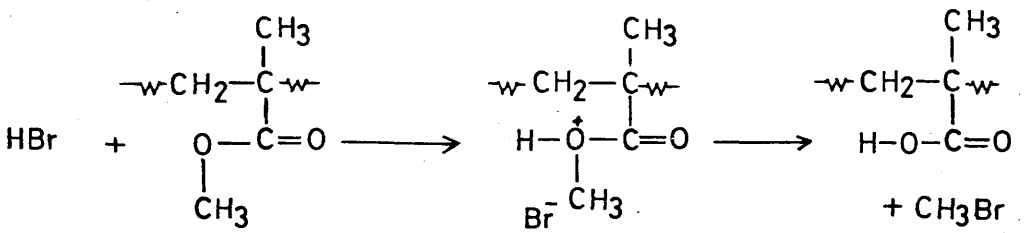
b. Methyl Bromide Formation

Zutty and Welch[33] suggested that the VB - M M A copolymer system is one of several in which degradation occurs by intramolecular lactonization involving adjacent vinyl halide and ester groups in the copolymer chain and the release of alkyl halide as a volatile product.



McNeill et al[34, 35, 36], suggested that HCl can convert the ester group in P M M A to methacrylic acid with evolution of CH_3Cl in the degradation both of VC - M M A copolymers and PVC - P M M A blends. In a recent study it was shown that methyl bromide is formed in the degradation of vinyl bromide-methyl methacrylate (VB - M M A) copolymers and PVB - P M M A blends[37], as well as lactone and anhydride structures which can have a stabilizing effect on the depolymerisation reaction. From Figure 5.18 it is shown that CH_3Br is formed at 280°C, which is the same temperature at which H Br is formed in the degradation of P2,3 - D B P M homopolymer.

It seems that H Br attacks the ester groups of M M A units with evolution of methyl bromide.



The data in Table 5.5 show that the highest value for methyl bromide is 5.1% for copolymer A_2 and from Figure 5.20 it is obvious that the maximum value lies in the range of copolymer composition between A_2 and A_3.

Table 5.11 presents data on the sequence distribution of monomer units in the copolymers obtained using a method developed by Harwood[38], which requires reactivity ratio values, monomer mixture and copolymer composition date. This statistical method shows that the maximum number of 2,3 - D B P M - M M A bonds occur at a copolymer composition of 50.5 - 49.5% 2,3 - D B P M - M M A. Thus it seems that the formation of methyl bromide is a direct function of the proportion

Table 5.11. Data on sequence distribution in copolymers A_1 , A_2 , A_3 , A_4 and A_5

Copolymer Composition A - B %	A - A bond in copolymer %	A - B and B - A bond in copolymer %	B - B bond in copolymer %	A-A-A triads (f_{AAA})	B-A-A and A-A-B triads (f_{BAA})	B-A-B triads (f_{BAB})
A_1 71.5-28.5	48.54	45.83	5.63	0.461	0.435	0.103
A_2 60 - 40	30.73	56.15	13.12	0.283	0.479	0.219
A_3 32 - 68	10.10	44.28	45.62	0.099	0.437	0.479
A_4 10 - 90	1.60	16.79	81.61	0.026	0.269	0.705
A_5 5 - 95	0.67	8.65	90.68	0.018	0.232	0.748

A : 2,3 - D B P M & B : M M A

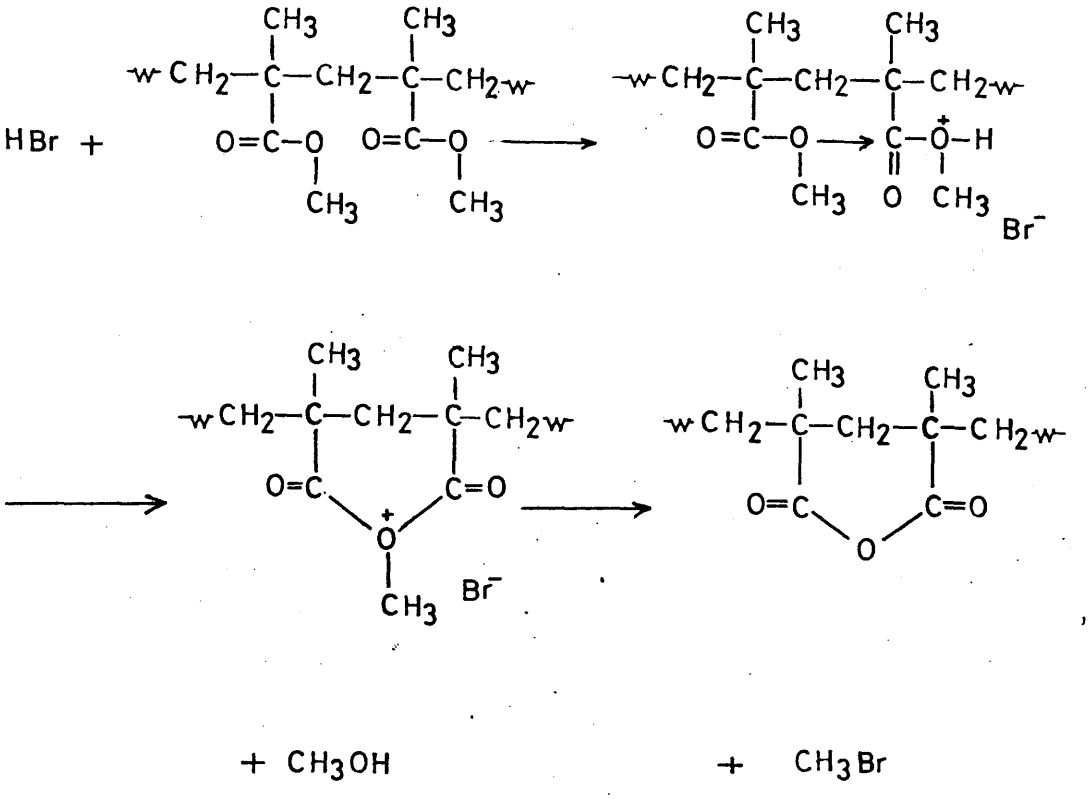
The symbol f denotes the fraction of A monomer to be found in the middle of the triads AAA, BAA and (AAB) and BAB.

of adjacent 2,3 - D B P M - M M A units in the copolymer.

c. Methanol Formation

McNeill and his colleagues[36] did not find methanol in the products of degradation of PVC - P M M A mixtures, nor did Zutty and Welch[33], in the degradation of PVC - P M M A blends. Methanol is formed in small amounts in the degradation of VB - M M A copolymers[37].

We have found methanol in the products of the second stage of degradation of 2,3 - D B P M - M M A copolymers with a maximum value of o.7% in copolymer A_2. Figure 5.18 shows that CH_3Br reaches maxima at 300°C and 360°C which suggests that there is another type of reaction which may occur to produce CH_3Br and CH_3OH. The following mechanism is proposed.



In this mechanism for the reaction between hydrogen bromide and M M A methyl bromide and methanol would be formed in equimolecular amounts. The additional CH_3Br would be formed in the reaction previously discussed. Methanol formation also reaches a maximum when the number of adjacent 2,3 - D B P M - M M A bond in the copolymer is at a maximum.

d. Of the products not so far discussed, polymethacrylic anhydride shows a maximum in the A_2 copolymer. The formation of this product can be satisfactorily explained by the reactions which produce CH_3Br alone, or CH_3Br and CH_3OH, which have just been described, as well as the reaction described in Chapter 4. Indeed, the formation of the anhydride structure in the copolymer chain has a stabilizing effect on the depolymerisation reaction. This is explained if these structures act as "blocking" groups which interrupt the unzipping process which, in P M M A, has a long zip length[30]. Thus the end - initiated depolymerisation is almost eliminated and the random - initiated depolymerisation requires a higher energy of activation. Other units incorporated into the P M M A chain can also have this property[39-42].

ii. 2,3 - D B P A - M M A Copolymer

a. As well as the formation of M M A monomer as a major product ranging from 18.2% to 80.7%, the yield of 2,3 - D B P A monomer is greater than in the degradation of P2,3 - D B P A homopolymer, ranging from 0.9 % to 2.2 %. Table 5.10 shows that 2,3 - D B P A monomer increases as the concentration of acrylate in the copolymer is decreased. It was observed by Grassie[24] that M A monomer is formed in high yield in the degradation of MA - M M A copolymers.

Table 5.12. Data on sequence distribution in copolymers A_6 , A_7 , A_8 , A_9 and A_{10}

Copolymer Composition A - B %	A - A bond in copolymer %	A - B and B - A bond in copolymer %	B - B bond in copolymer %	A-A-A triads (f_{AAA})	B-A-A and A-A-B triads (f_{BAA})	B-A-B triads (f_{BAB})
A_6 56-44	26.4	59.20	14.40	0.222	0.498	0.279
A_7 42-58	12.27	55.45	32.27	0.085	0.414	0.501
A_8 18-82	1.71	32.58	65.71	0.009	0.172	0.519
A_9 14-86	1.28	25.44	73.28	0.008	0.166	0.826
A_{10} 9-91	0.16	17.68	82.16	0.003	0.035	0.965

A : 2,3 - D B P A & B : M M A

The symbol f denotes the fraction of A monomer to be found in the middle of the triads AAA, BAA and (AAB) and BAB.

It seems that single acrylate units can readily participate in an unzipping process but that unzipping cannot pass through groups of 2,3 - D B P A units.

b. Methyl Bromide, Methanol and Anhydride Formation

The mechanisms resulting in the formation of these products should be expected to be identical to those already presented in the discussion of the degradation of 2,3 - D B P M - M M A copolymer. CH_3Br and CH_3OH production show maxima of 22.3% and 1.5% respectively from copolymer A_6. The cold ring fraction shows a maximum of 27.5% from copolymer A_6. Table 5 . 12 shows that the maximum proportion of 2,3 - D B P A - M M A bonds occurs in copolymer A_6, which yield the highest percentages of these products. The formation of high yield of anhydride structure may stabilize copolymer A_6 more than the others.

CHAPTER 6

THERMAL DEGRADATION of 2,3 - D B P M - S and 2,3 - D B P A - S COPOLYMERS

6. 1 INTRODUCTION

It has been shown in the previous chapter that the thermal degradation behaviour of 2,3 - D B P M and 2,3 - D B P A units can be greatly influenced by the presence of M M A groups in the polymer chain.

The thermal degradation of polystyrene involves both depropagation and transfer reactions. The degradation products typically contain monomer comprising 42% of the original sample weight, with progressively decreasing amounts of dimer, trimer, tetramer, pentamer and small amounts of toluene and benzene[43]. Copolymers of 2,3 - D B P M - S and 2,3 - D B P A - S were therefore studied, in order to determine whether any interaction between the monomer units takes place during the degradation process. In this chapter the thermal degradation of these copolymers will be described, their degradation products reported either qualitatively or quantitatively, and finally their stability and degradation mechanisms discussed.

6. 2 THERMAL DEGRADATION of 2,3 - D B P M - S COPOLYMERS

i. Molecular Weights

Number Average Molecular Weights were measured by the method outlined in chapter 2. Five 2,3 - D B P M - S copolymers were prepared containing the following mole % of 2,3 - D B P M :

63% (A_{11}), 55% (A_{12}), 31% (A_{13}), 23% (A_{14}) and 13% (A_{15}).

Table 6 . 1 lists the Number Average Molecular Weights of these copolymers.

Table 6. 1. Number Average Molecular Weights of 2,3 - D B P M - S Copolymers

2,3 - D B P M - S	$\overline{M}_n$
A_{11}	538,000
A_{12}	316,000
A_{13}	182,000
A_{14}	153,000
A_{15}	95,000

ii. Thermal Volatilisation Analysis (T V A)

The copolymers were examined in the form of a white powder with sample size 50 mg. They were heated from ambient temperature to 500°C at 10°C/min under normal T V A conditions. The T V A traces of the copolymers A_{11} , A_{12} , A_{13} , A_{14} and A_{15} are shown in figures 6.1, 6.2, 6.3, 6.4 and 6.5 respectively. At higher 2,3 - D B P M contents, the T V A traces reveal a relatively sharp main peak followed by a small broad peak. At higher styrene contents, there are two distinct peaks. Volatilisation starts between 230° - 255°C and reaches T_{max} at 325°C and again at 396°C. All the traces are separated to some extent, suggesting that products with a range of volatilities are being evolved. The -196°C trace indicates that a non-condensable fraction is also being formed at an early stage. The cold ring fraction was coloured deep yellow and was dissolved in chloroform for infra-red spectroscopic analysis. A small amount of residue remained at 500°C.

iii. T G and D S C

The weight loss curves for the five copolymers are shown in figure

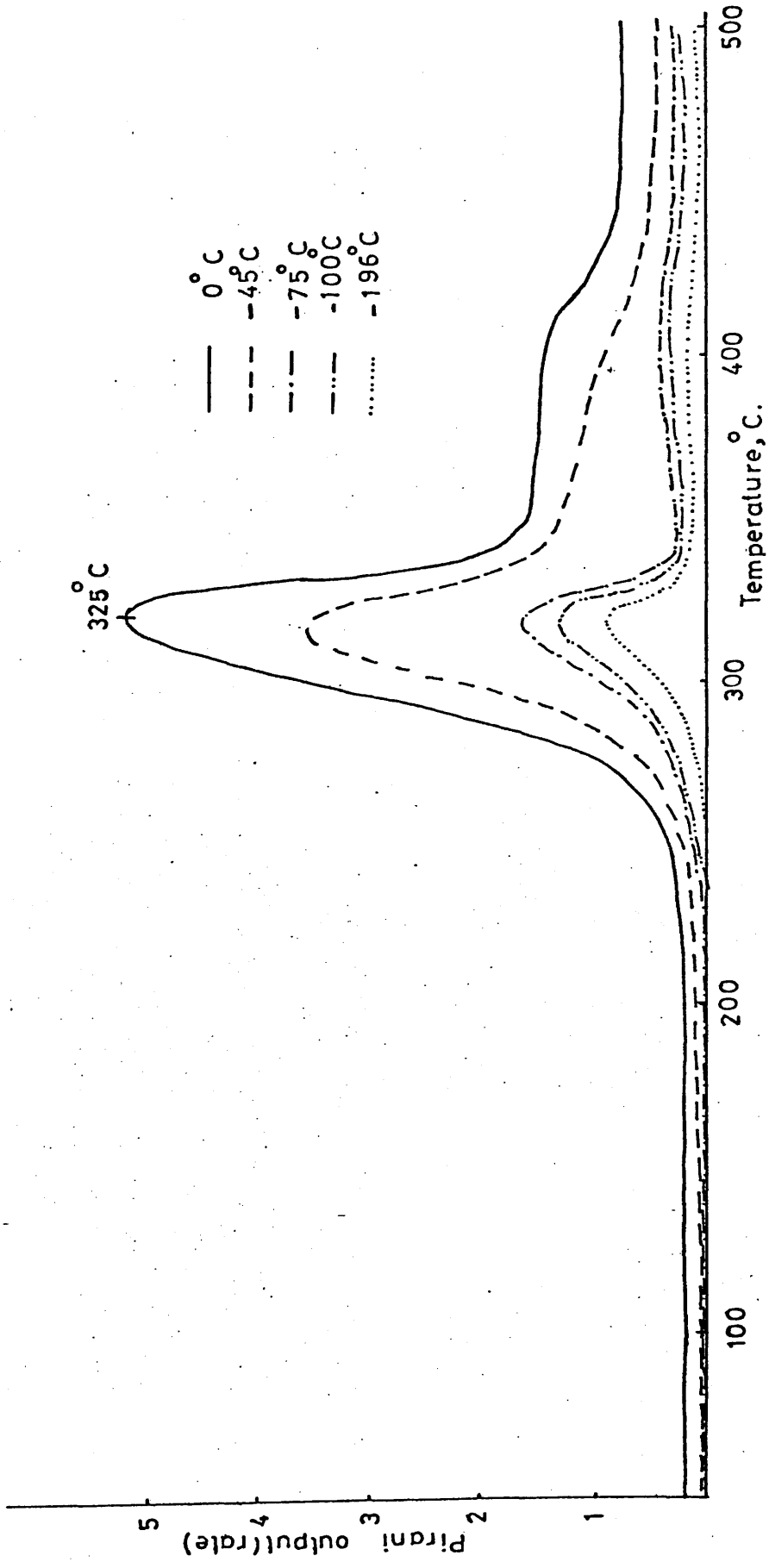


Fig.6.1. T V A thermogram of A_{11} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

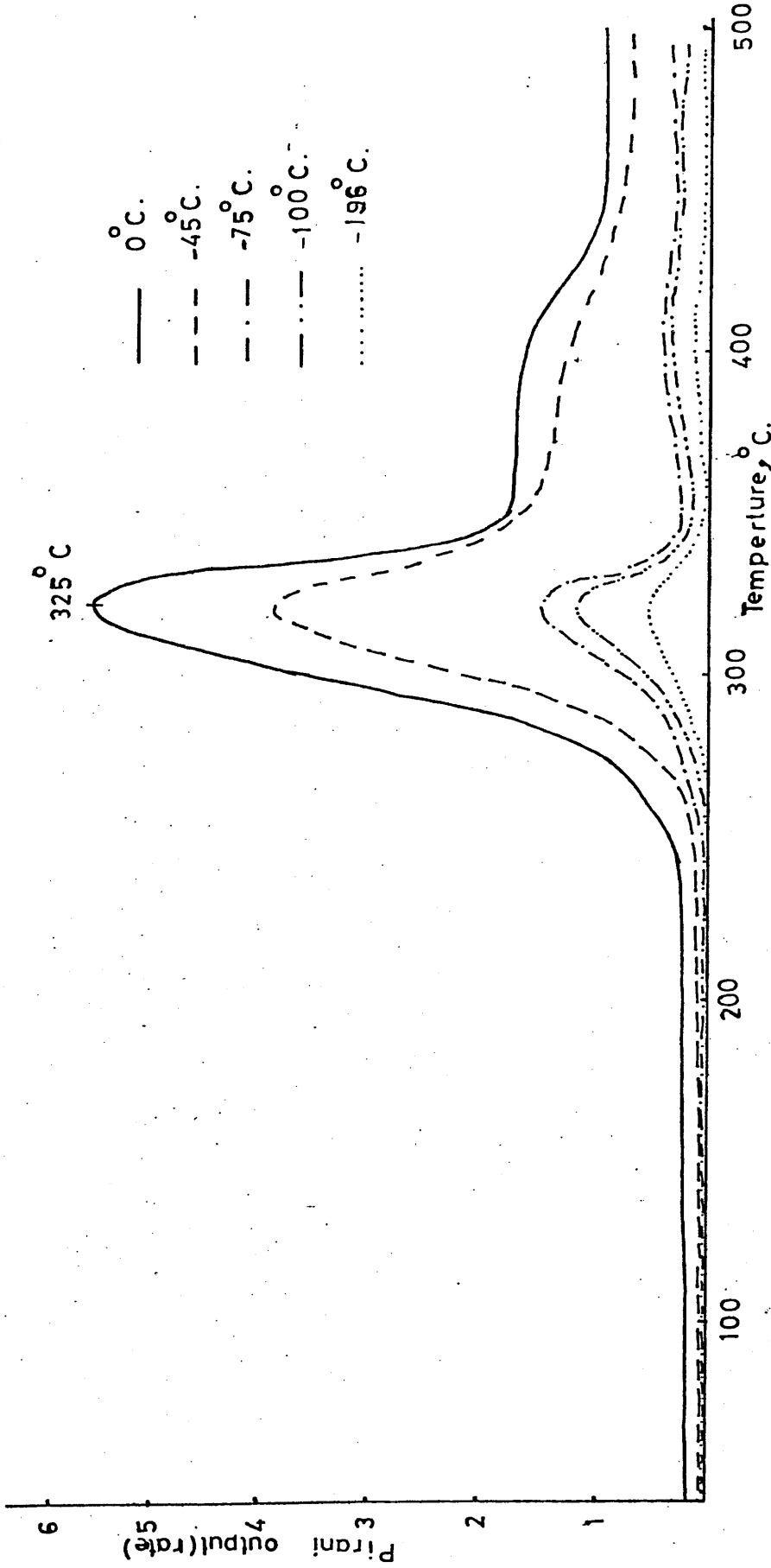


Fig.6.2. T V A thermogram of A_{12} copolymer , sample size 50 mg ; heating rate 10°/min.

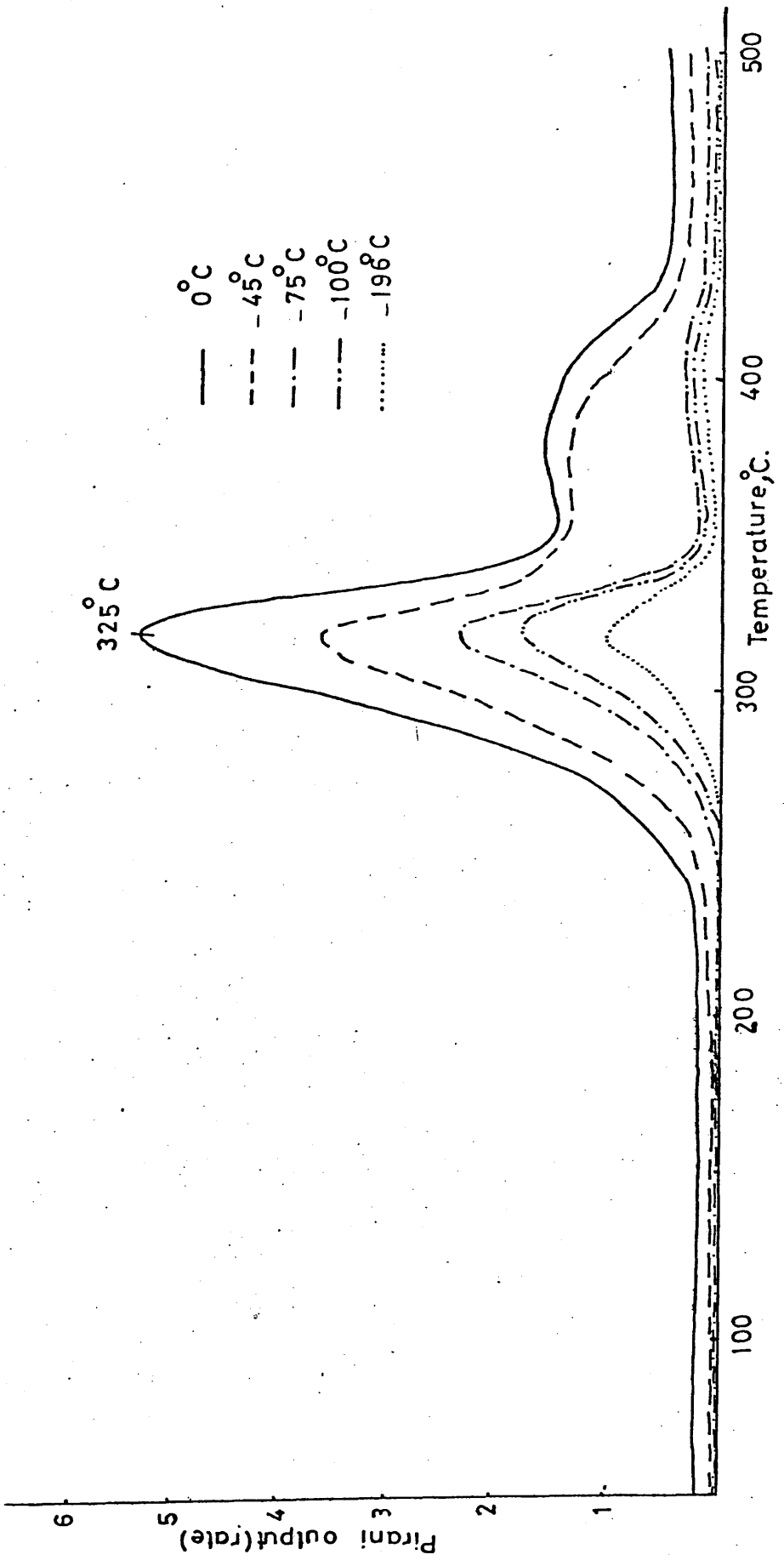


Fig. 6.3. T V A thermogram of A_{13} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

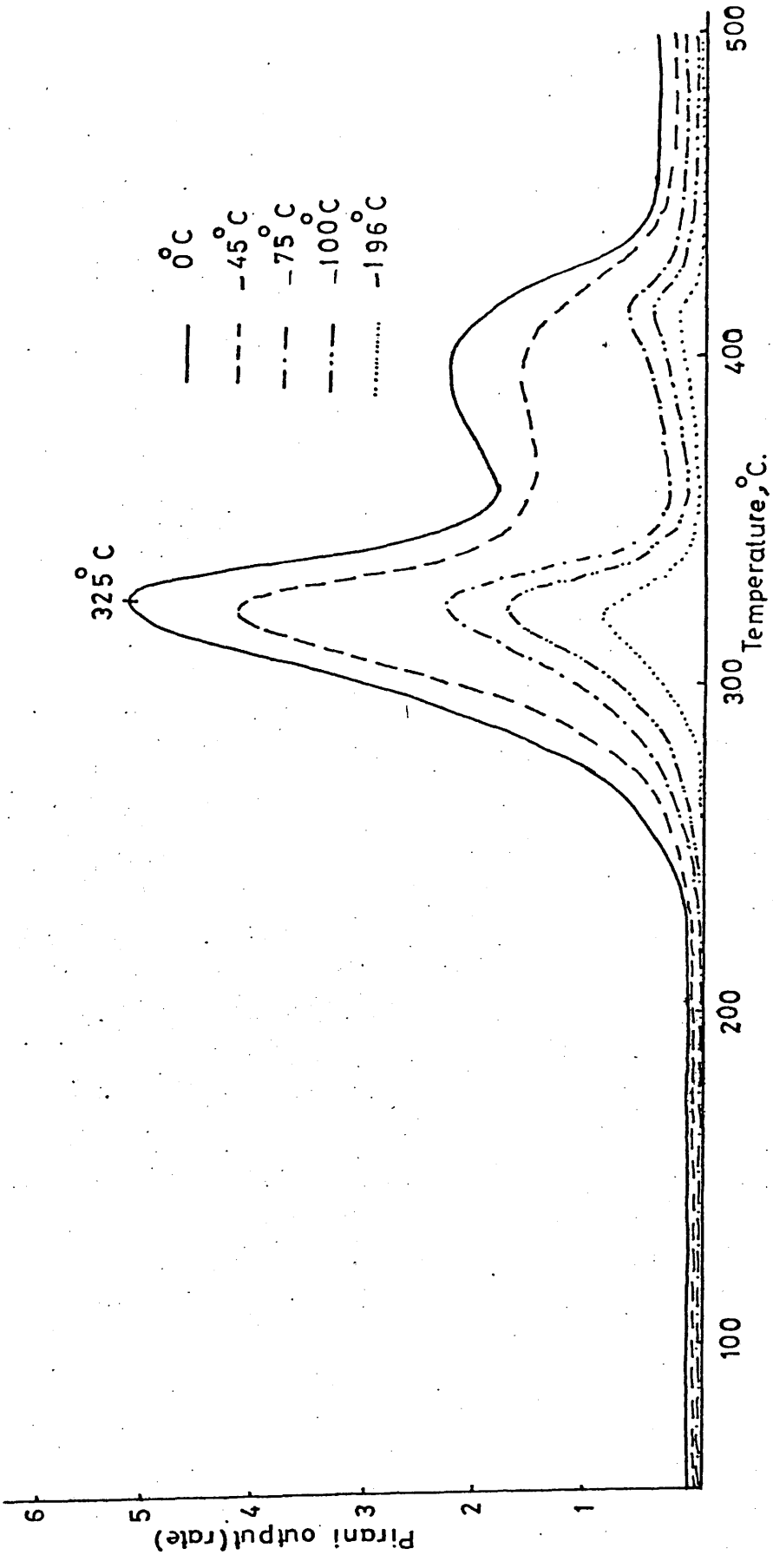


Fig. 6.4. T V A thermogram of A_{14} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

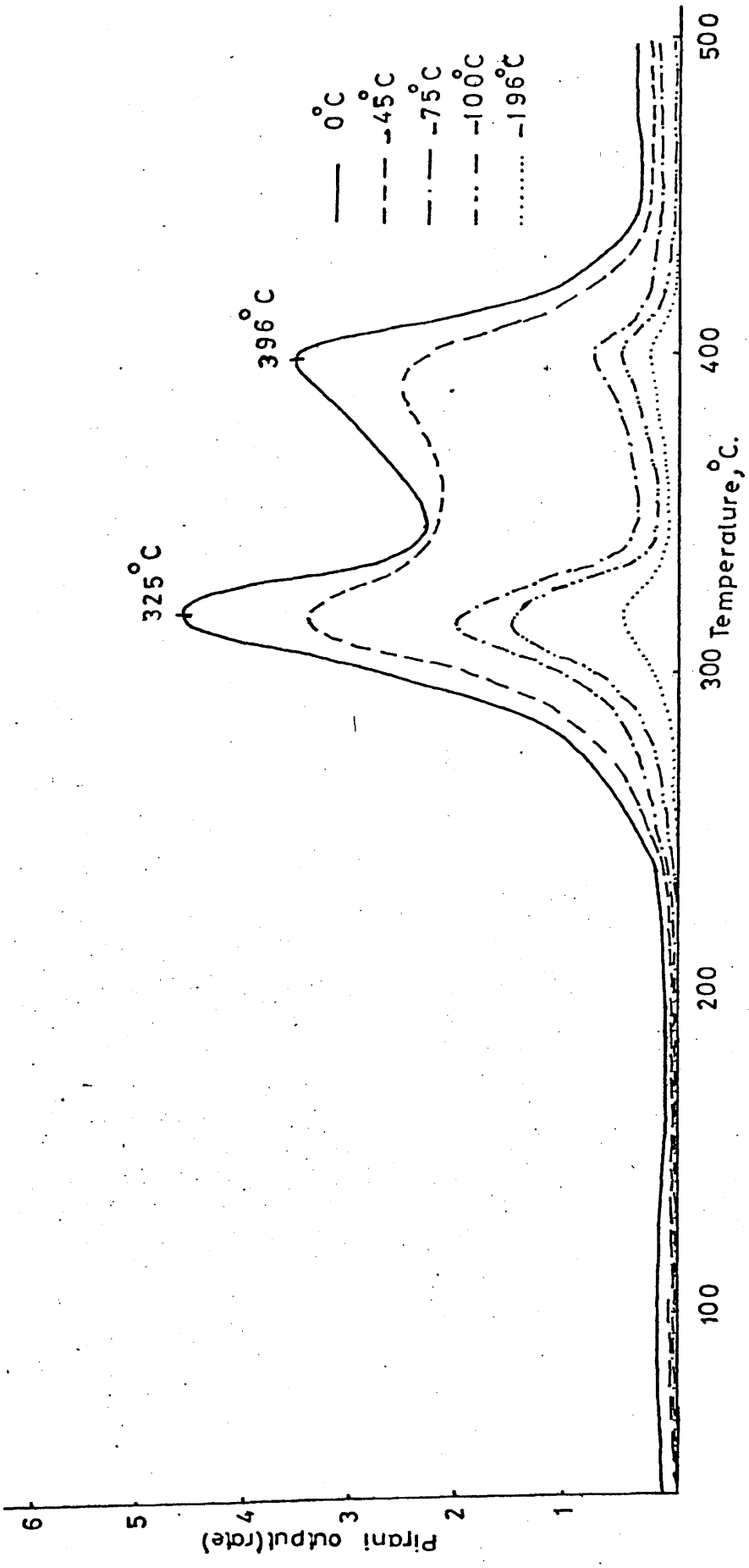


Fig.6.5. T V A thermogram of A_{15} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

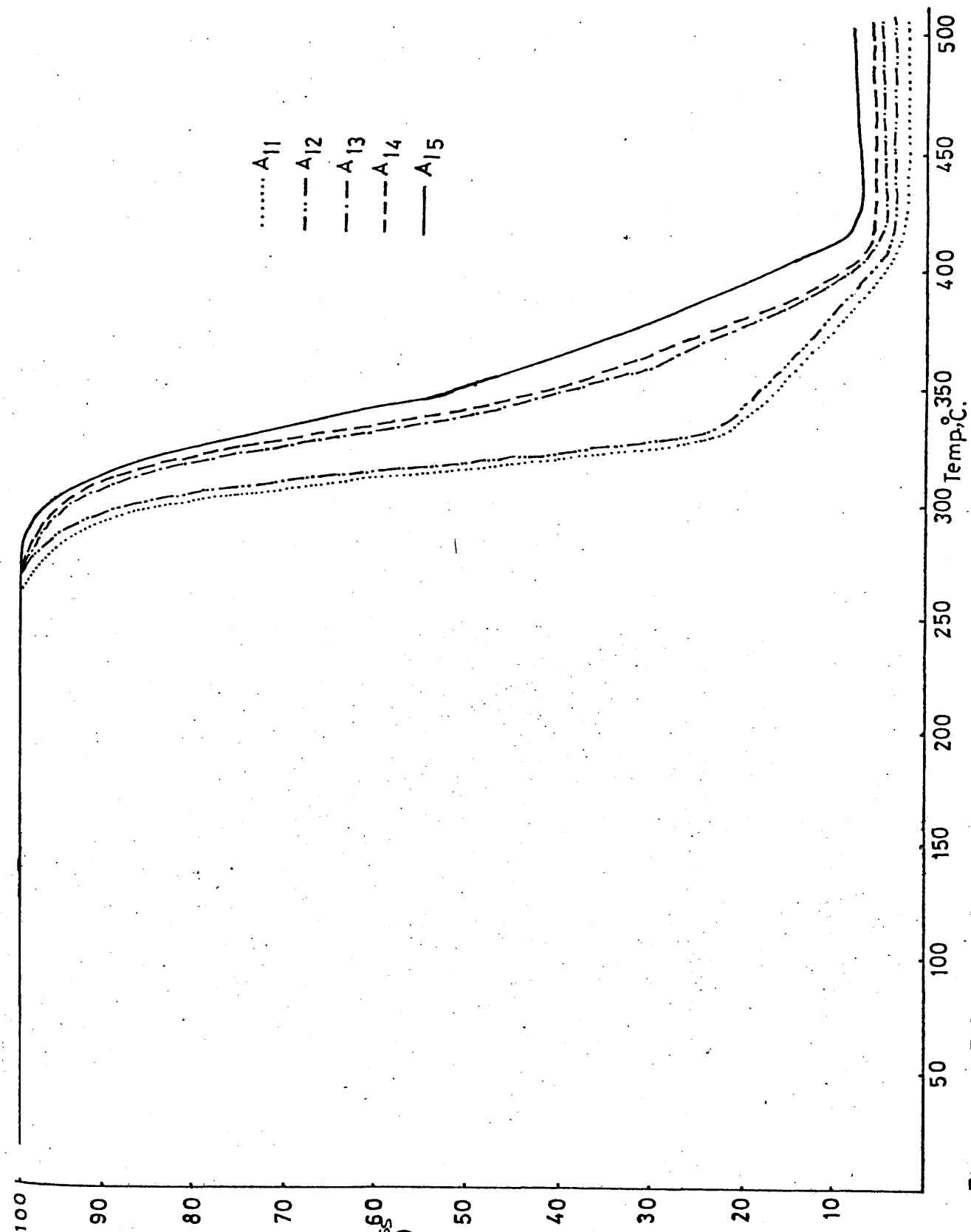


Fig. 6.6. T G curves for 2,3 - D B P M - S copolymers.

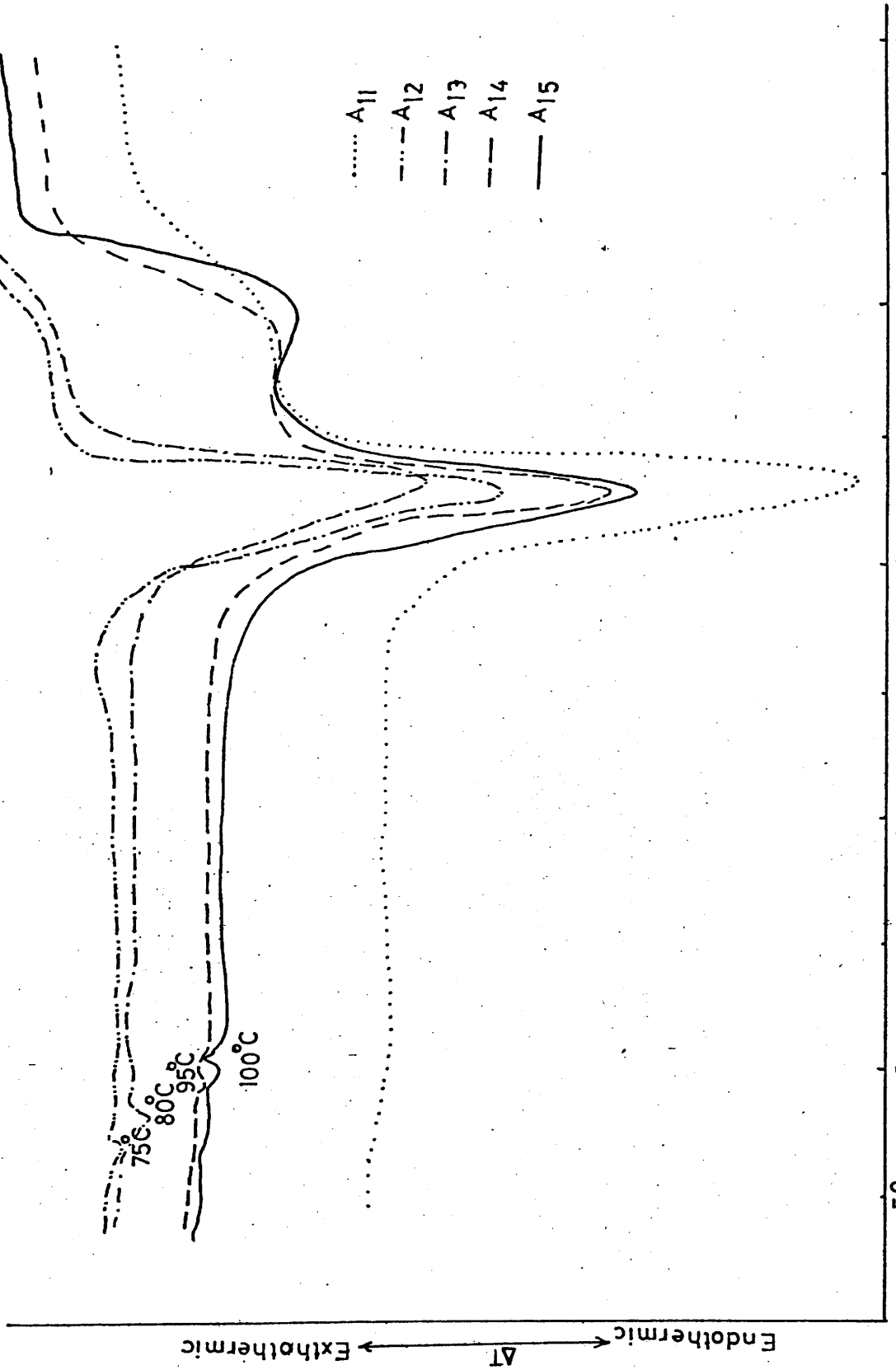


Fig. 6.7. D S C traces for 2,3 - D B P M - S copolymers.

6.6. The sample was heated at 10° per minute from ambient temperature to 500°C. Weight loss starts between 225°-250°C and occurs in a two stage process, the relative importance of each stage being dependant on the copolymer composition. Table 6. 2 shows the percentage weight loss of each copolymer in each stage. The stability of the copolymer increases as the styrene content of the copolymer increases.

D S C curves for these copolymers(figure 6.7) show two endothermic peaks, the relative size of the peaks being dependant upon copolymer composition. The glass transition temperatures, T_g, of the copolymers decrease as 2,3 - D B P M content increases.

Table 6. 2. Percentage Weight Loss of 2,3 - D B P M - S Copolymers
Sample heated at 10° per minute from ambient temperature to 500°C

Polymer	First Stage	Second Stage
A_{11}	80	18
A_{12}	75	21
A_{13}	65	32
A_{14}	55	35
A_{15}	48	40

iv. Subambient T V A and Product Analysis

Subambient T V A was carried out using 50 mg samples of the copolymers. Each sample was heated from ambient temperature to 500°C at 10°/min under normal subambient T V A conditions, as described in Chapter 2. Figure 6.8 shows the subambient T V A trace of the copolymer A_{13}.

I r , mass spectrometry and g l c were used to examine these condensable degradation products with the results shown in figures 6.9 and

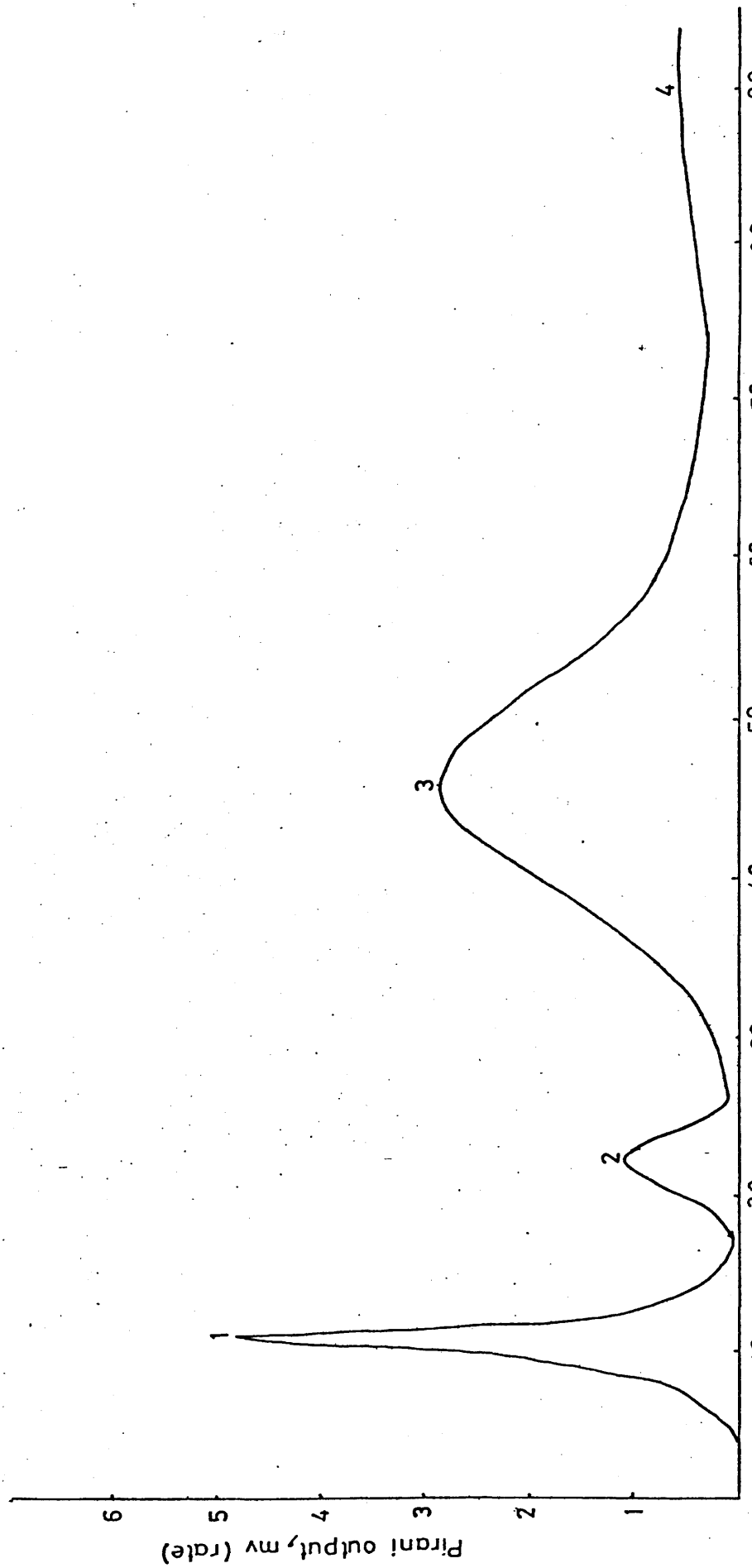


Fig. 6.8. S A T V A trace for the degradation products of 2,3 - D B P M - S copolymer (A_{13}) from programmed degradation under vacuum to 500°C at 10°/min , 50 mg sample.

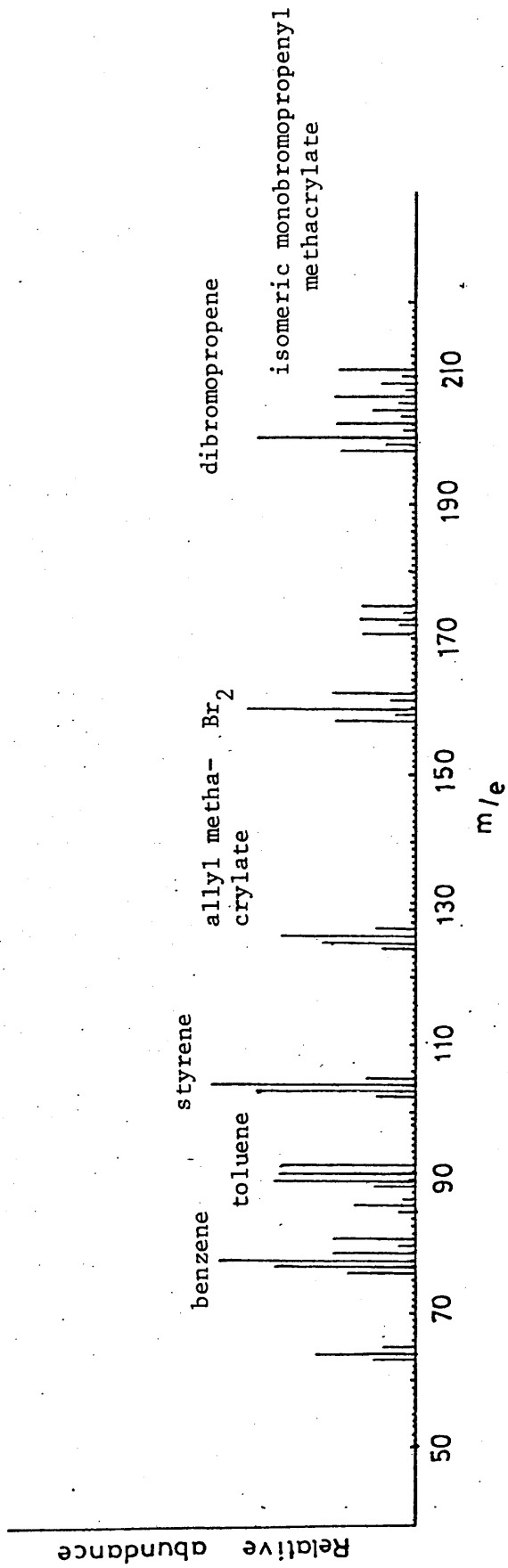


Fig. 6.9. Mass spectrum of peak 3 of the S A T V A of 2,3.- D B P M - S degradation.

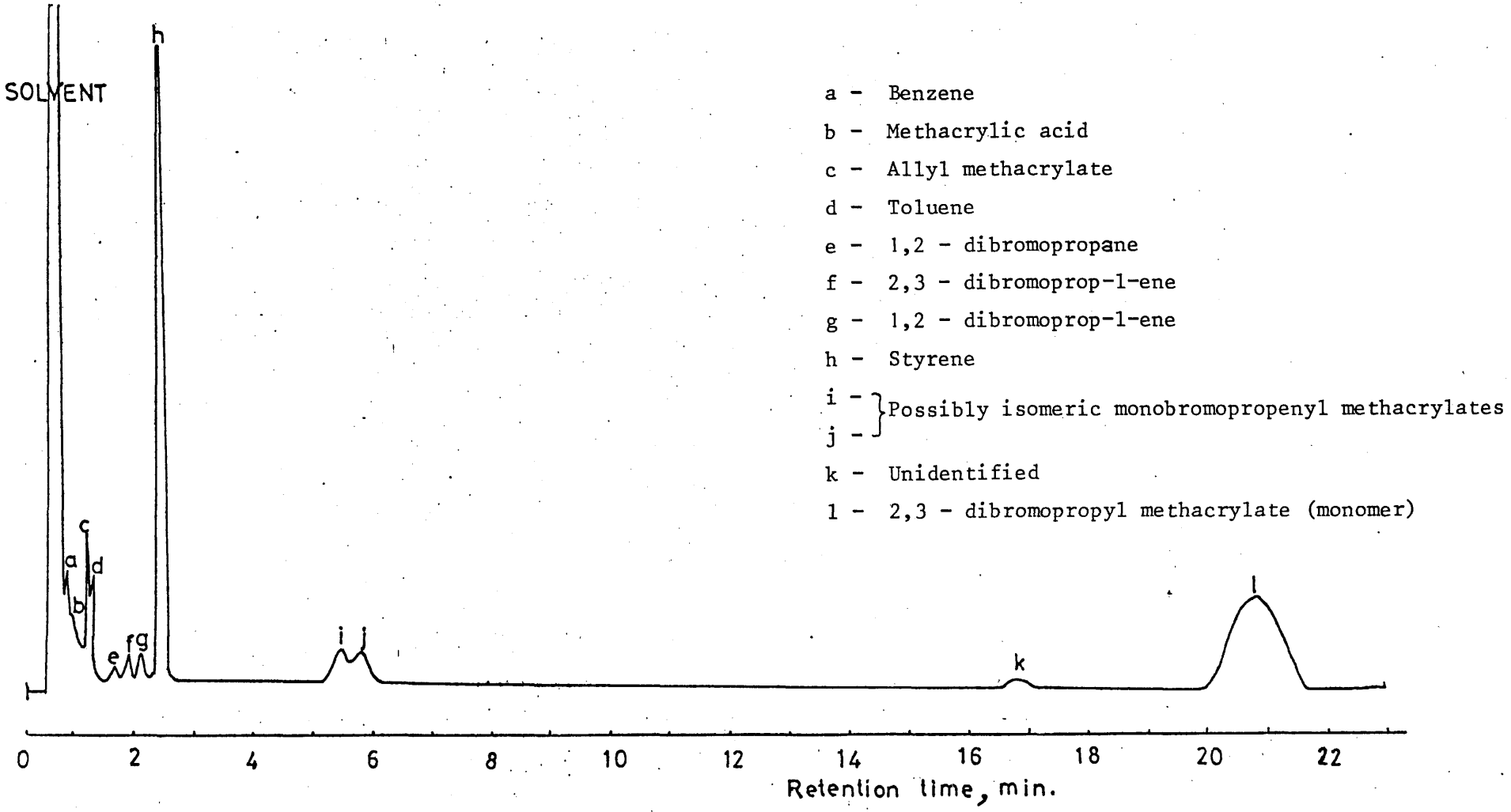
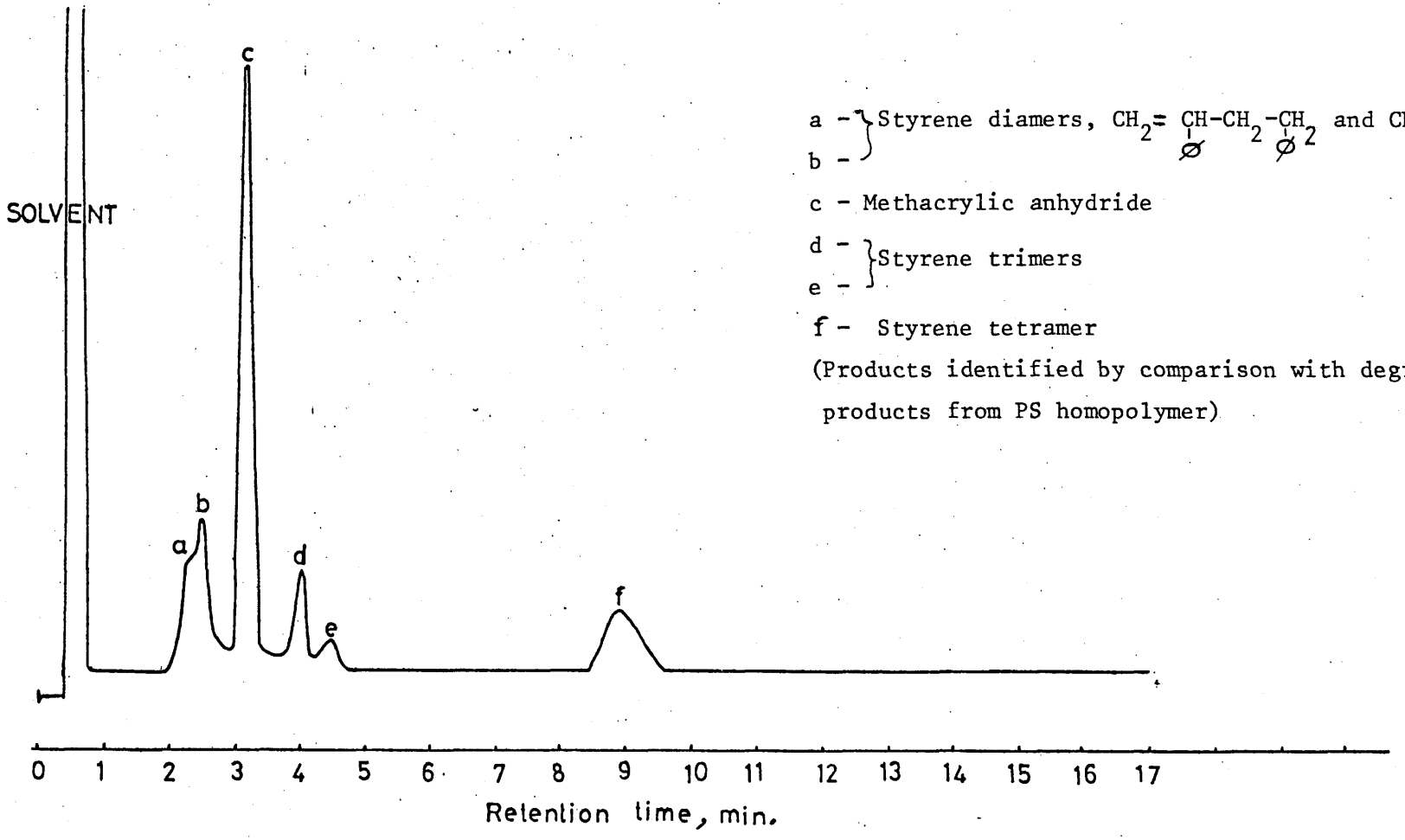


Fig.6.10. G L C trace for the degradation products of peaks 3 and 4 in the subambient T V A curve (figure 6.8) using 5 ft. ¼ inch diameter, 10% microwax on chromosorb column isothermally at 140°C.



a - } Styrene diamers, $CH_2=\underset{\varnothing}{CH}-CH_2-\underset{\varnothing}{CH_2}$ and $CH_3-\underset{\varnothing}{CH}=CH-\underset{\varnothing}{CH_2}$
b - }

c - Methacrylic anhydride

d - } Styrene trimers
e - }

f - Styrene tetramer

(Products identified by comparison with degradation products from PS homopolymer)

Fig. 6.11. G L C trace for C R F of 2,3 - D B P M - S copolymersafter 500°C, using 10 ft. $\frac{1}{4}$ inch diameter 1% OV1 on chromosorb column isothermally at 250°C.

Table 6. 3. Degradation products of 2,3 - D B P M - S Copolymers from ambient temperature to 500°C at 10°/min.

Degradation fraction	Products	Method of Analysis
Non-condensable materials	CH_4 , CO and propene	I R & M S
C R F	Polymethacrylic anhydride + dimer, trimer, tetramer pentamer of styrene	I R in solution and g l c
Residue	Carbon	I R (K Br disc)
Condensable materials:		
Peak 1 (S A T V A)	CO_2 , HBr	I R & M S
Peak 2 (S A T V A)	Allyl bromide	I R & M S
Peak 3 (S A T V A)	Benzene, toluene, styrene, H_2O , Br_2 , methacrylic acid, allyl methacrylate, 1,2 - dibromopropane, Isomeric dibromopropenes, Isomeric monobromopropenyl methacrylates*	I R, M S and g l c
Peak 4 (S A T V A)	2,3 - dibromopropyl methacrylate (monomer)	M S & g l c

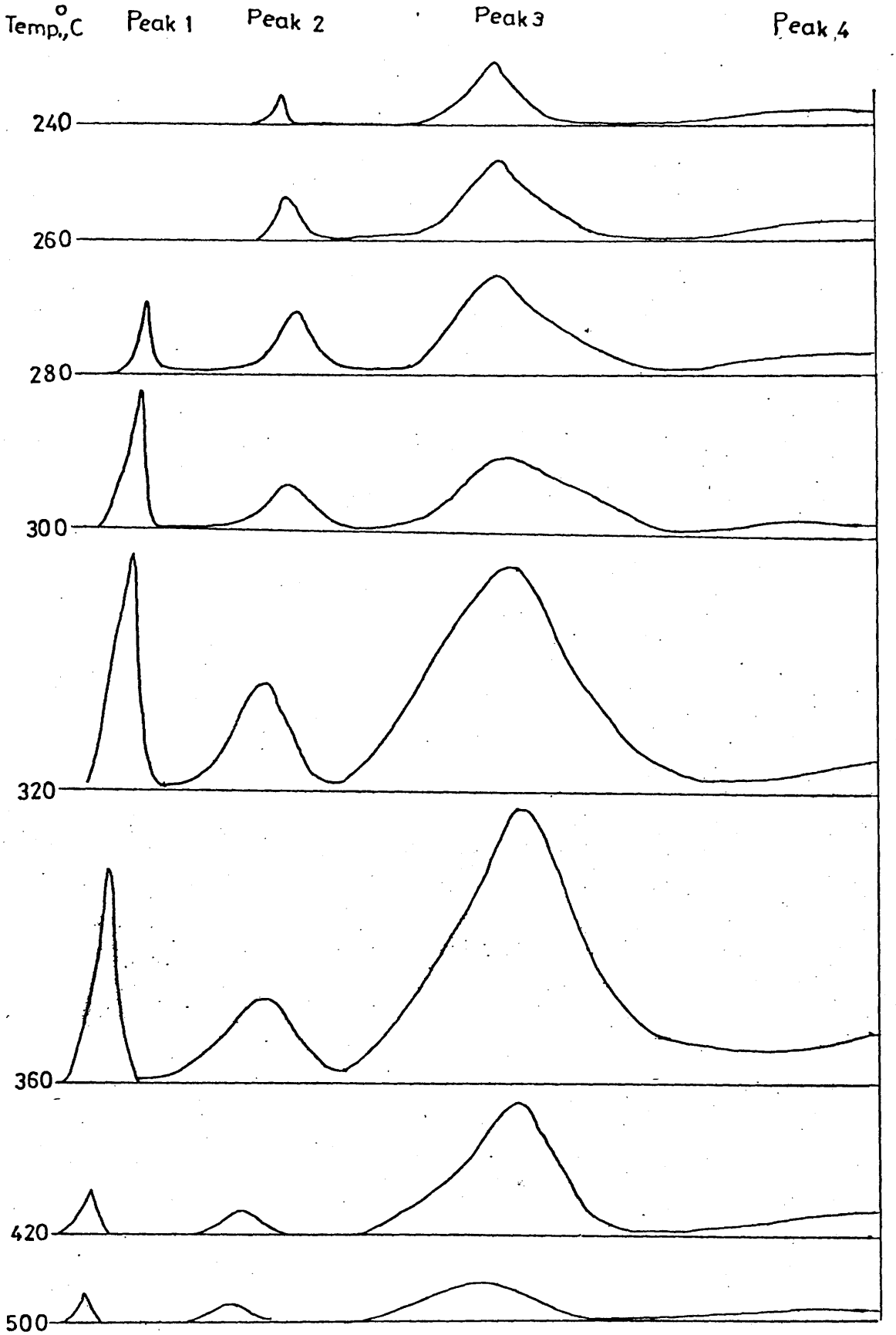


Fig. 6.12. Subambient T V A curves for the degradation of a single sample of A_{13} (for programmed degradation under vacuum from ambient to successively higher temperature at 10^{o}/min , 50 mg sample size). Sample held at each temperature while products were collected

6.10. The non-condensable materials were collected in a closed system and were examined by i r and mass spectrometry. Cold ring fractions were examined by i r in chloroform solution, and g l c (figure 6.11). The degradation products of the 2,3 - D B P M - S copolymers have been identified to the extent shown in Table 6. 3. As before, the identity of products indicated by * is tentative. The stepwise degradation procedure described in Chapter 4, was carried out on a single sample of A_{13} copolymer in the S A T V A apparatus. The temperature of the stages ranged from 240°C to 500°C, and figure 6.12 shows the series of S A T V A curves obtained. Peak 1 first appeared at a much higher temperature than the other three peaks as in the degradation of 2,3 - D B P M and 2,3 - D B P A homopolymers; up to 320°C, peak 1 consists of HBr only, after which CO_2 is formed continuously to 500°C. No HBr was formed above 420°C.

v. Quantitative Measurement of Degradation Products

Infra-red spectroscopy and g l c were used for quantitative analysis of the degradation products as described in Chapter 2. I r was used for peaks 1 and 2 in the S A T V A and g l c for peaks 3 and 4 Table 6. 4 lists the quantitative analysis of the degradation products of 2,3 - D B P M - S copolymers to 500°C at 10°/min. Values marked * are tentative.

Table 6.. 4. Quantitative Analysis of the Products of Degradation of 2,3 - D B P M - S Copolymers (20^{o}- 500^{o}C , at 10^{o}C/min)

Product	A_{11}	A_{12}	A_{13}	A_{14}	A_{15}
	Wt.(%)				
HBr	7.5	6.3	5.0	2.5	1.3
CO_2	1.49	1.27	0.72	0.43	0.4
Propene	0.2	0.2	0.15	0.1	trace
Allyl bromide	1.6	1.31	0.83	0.51	0.43
Benzene	trace	trace	trace	trace	trace
H_2O	trace	trace	trace	trace	trace
Br_2	1.6	1.3	1.0	0.6	0.3
Toluene	trace	trace	trace	trace	trace
Methacrylic acid	trace	trace	trace	trace	trace
Allyl methacrylate	1.1	0.8	0.5	0.3	0.2
1,2 - dibromopropane	0.1	trace	-	-	-
Isomeric dibromopropenes	0.3	0.2	trace	-	-
Styrene (monomer)	12.01	16.37	27.31	31.26	36.17
Isomeric monobromopropenyl methacrylates	0.7 *	0.6 *	0.3 *	0.2 *	0.1 *
2,3 - dibromopropyl methacrylate(monomer)	33.5	30.2	16.36	12.91	5.88
C R F	27.3	32.0	42.7	46.2	51.9
Residue	5	4	4	2	2
Total products identified	92.4	94.55	98.87	97.01	98.68

6. 3 THERMAL DEGRADATION of 2,3 - D B P A - S COPOLYMERS

i. Molecular Weights

Five copolymers were prepared as described in Chapter 2, the polymerisation being stopped at 5% conversion. The mole % of 2,3 - D B P A in the five copolymers was as follows : 57% (A_{16}), 48% (A_{17}), 29% (A_{18}), 21% (A_{19}), 17% (A_{20}). Table 6. 5 shows the Number Average Molecular Weights of these copolymers.

Table 6. 5. Number Average Molecular Weights of 2,3 - D B P A - S Copolymers

Polymer	$\overline{M}_n$
A_{16}	248,000
A_{17}	212,000
A_{18}	187,000
A_{19}	159,000
A_{20}	148,000

ii. Thermal Volatilisation Analysis (T V A)

Figures 6.13, 6.14, 6.15, 6.16 and 6.17 show the T V A traces for the A_{16}, A_{17}, A_{18}, A_{19} and A_{20} copolymers respectively. In each case there is a sharp peak followed by a low broad peak and the relative sizes of the peaks are dependant on the copolymer composition. Volatilisation starts at 233°C and reaches maxima at 330°C and again at 397°C. The separation of the curves shows that there are products of a wide range of volatilites and a considerable amount of material

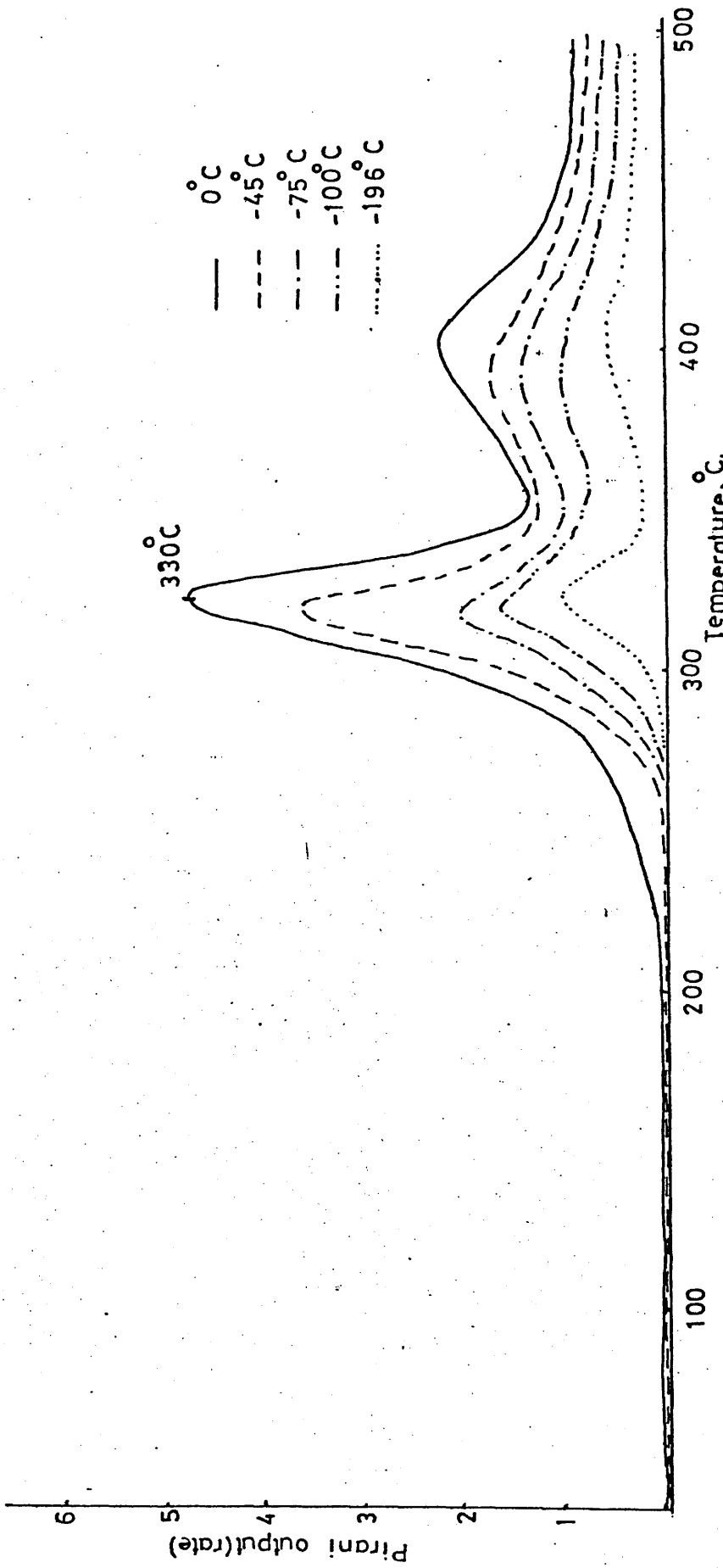


Fig. 6.13. T V A thermogram of A_{16} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

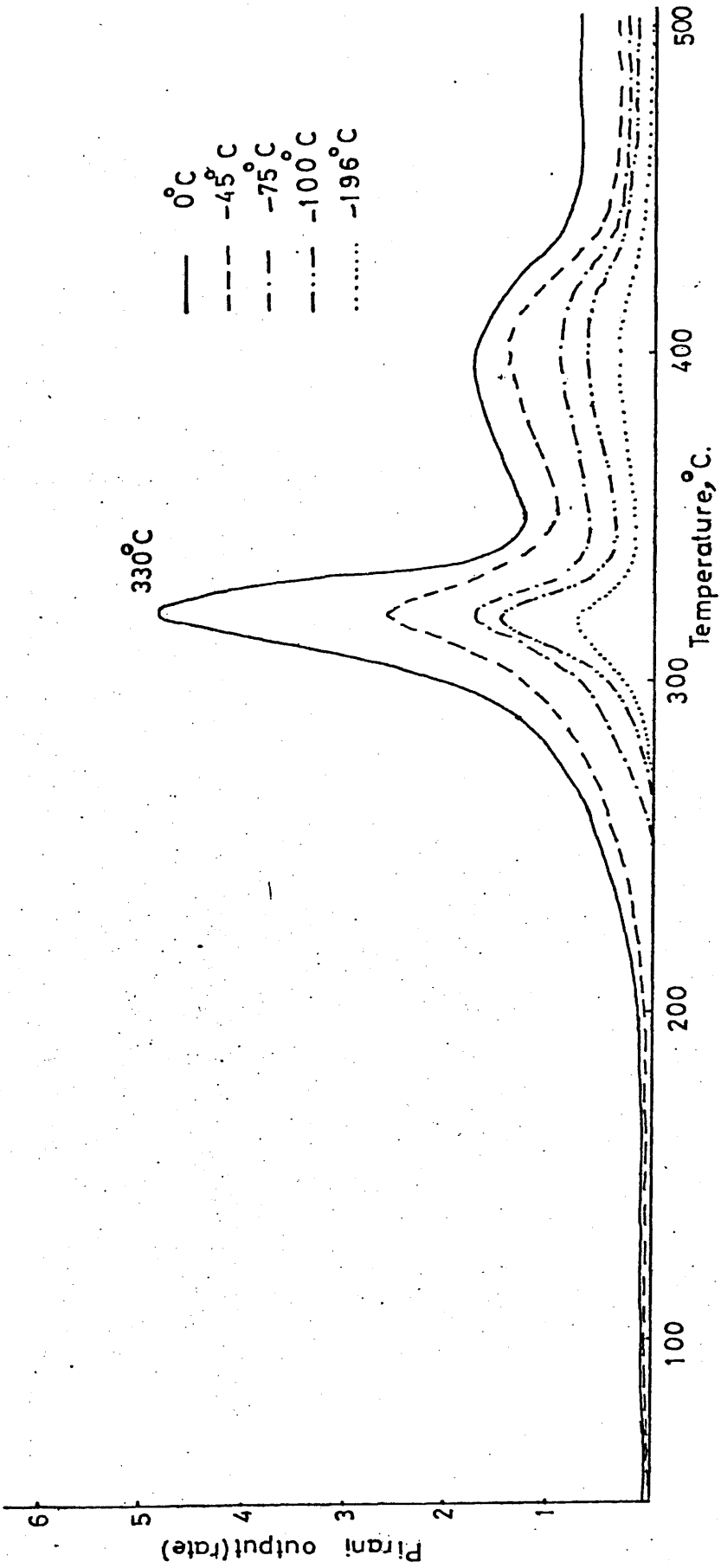


Fig. 6.14. T V A thermogram of A_{17} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

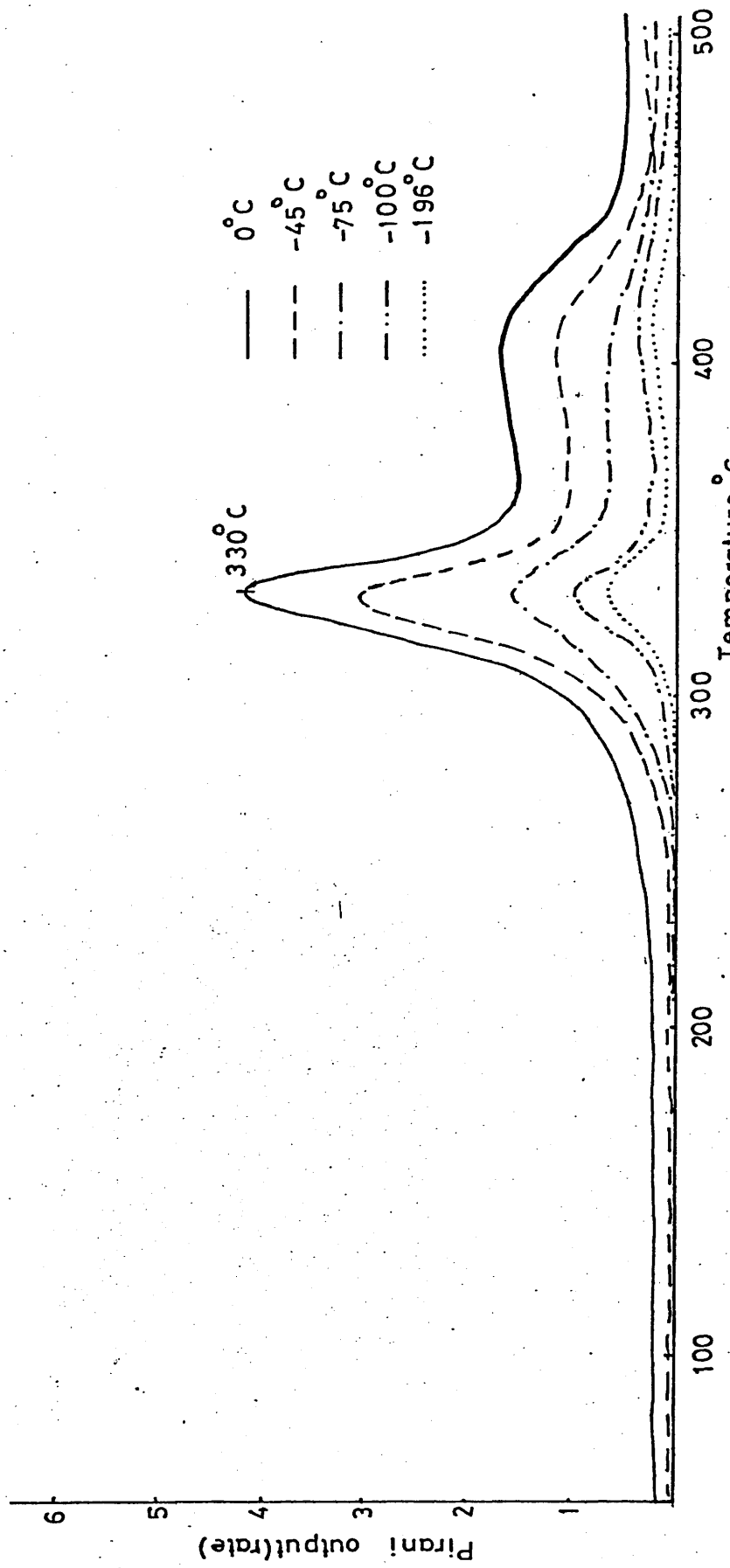


Fig.6.15. T V A thermogram of A_{18} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

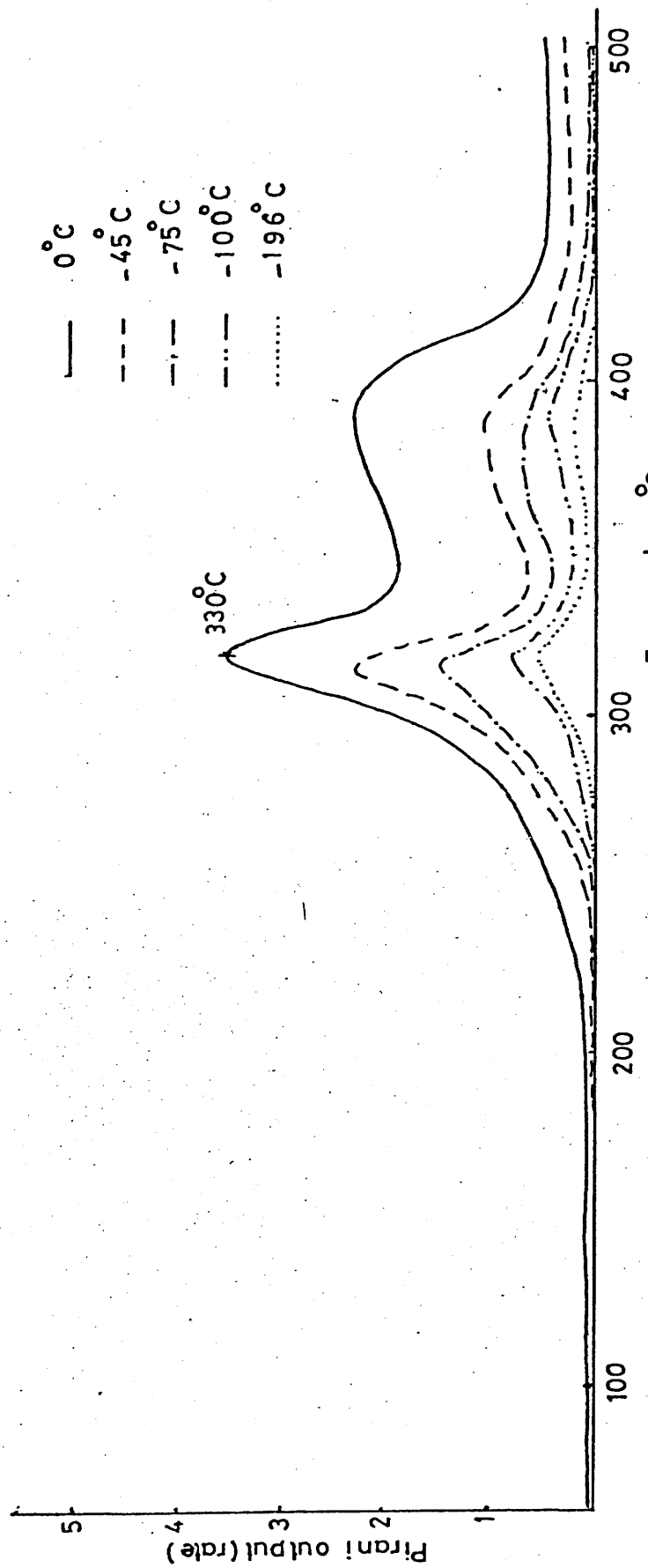


Fig.6.16. T V A thermogram of A_{19} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

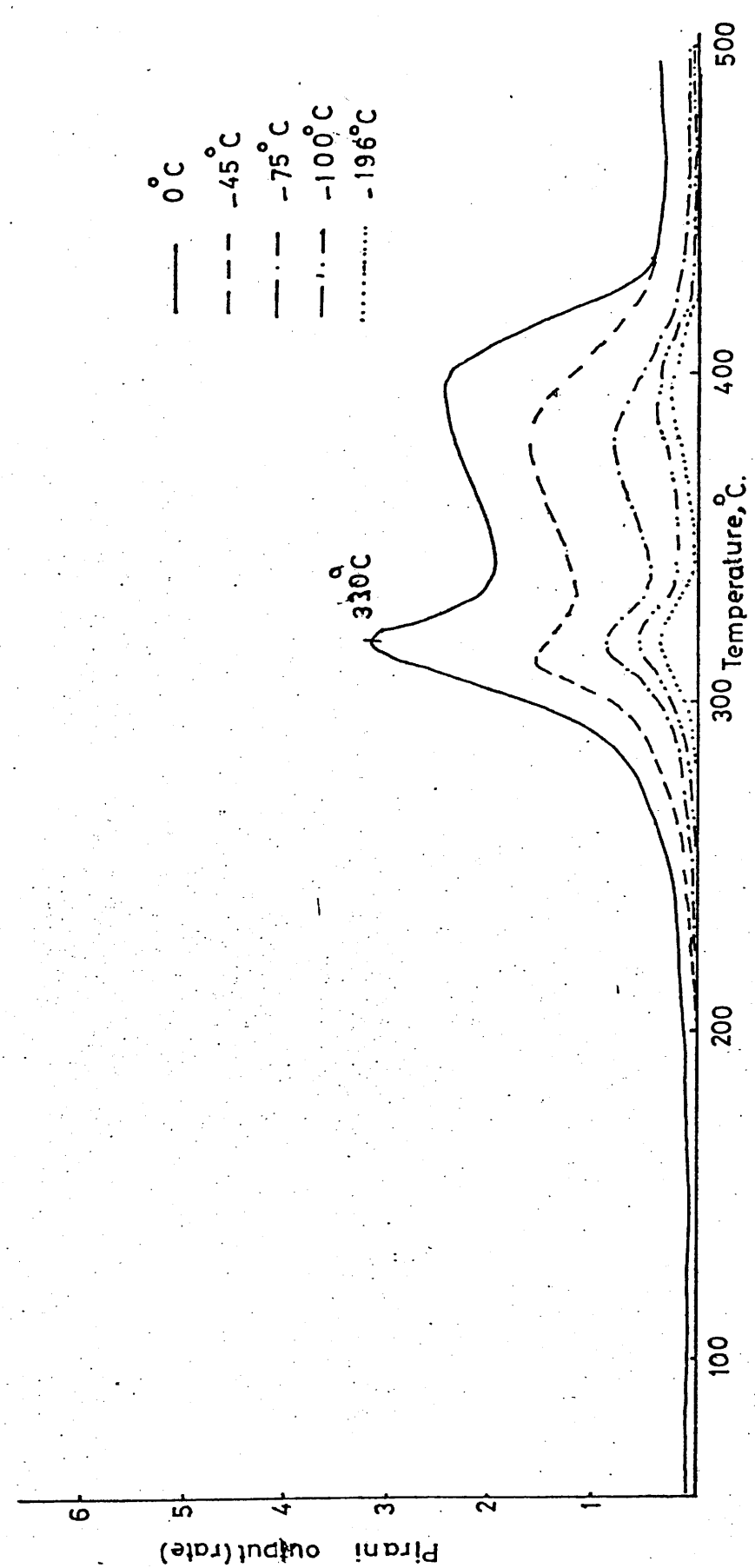


Fig. 6.17. T V A thermogram of A_{20} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

is non-condensable at -196°C. A yellow cold ring fraction is formed and may be dissolved in chloroform for i r analysis. A small amount of residue remains at 500°C.

iii. T G and D S C

Figure 6 . 18 shows the T G traces of the five 2,3 - D B P A - S copolymers (A_{16}, A_{17}, A_{18}, A_{19} and A_{20}) obtained under the same conditions as described earlier for the 2,3 - D B P M - S copolymers. For the three copolymers of highest 2,3 - D B P A concentration, the T G curves, obtained under nitrogen (50 ml/min), have two distinct stages. Table 6 . 6 shows the percentage weight loss of the copolymers in each stage. The stability of the copolymer increases with increasing styrene content.

Table 6 . 6. Percentage Weight Loss of 2,3 - D B P A - S Copolymers
Samples heated at 10° per minute from ambient temperature to 500°C

Polymer	First Stage	Second Stage
A_{16}	64	27
A_{17}	60	31
A_{18}	50	42
A_{19}	94	-
A_{20}	87	-

D S C curves of the copolymers (figure 6 . 19) show in the case of the three copolymers of highest styrene content, two endothermic peaks between 320°- 330°C and 360°- 375°C respectively. The two copolymers of highest 2,3 - D B P A content give only the single lower

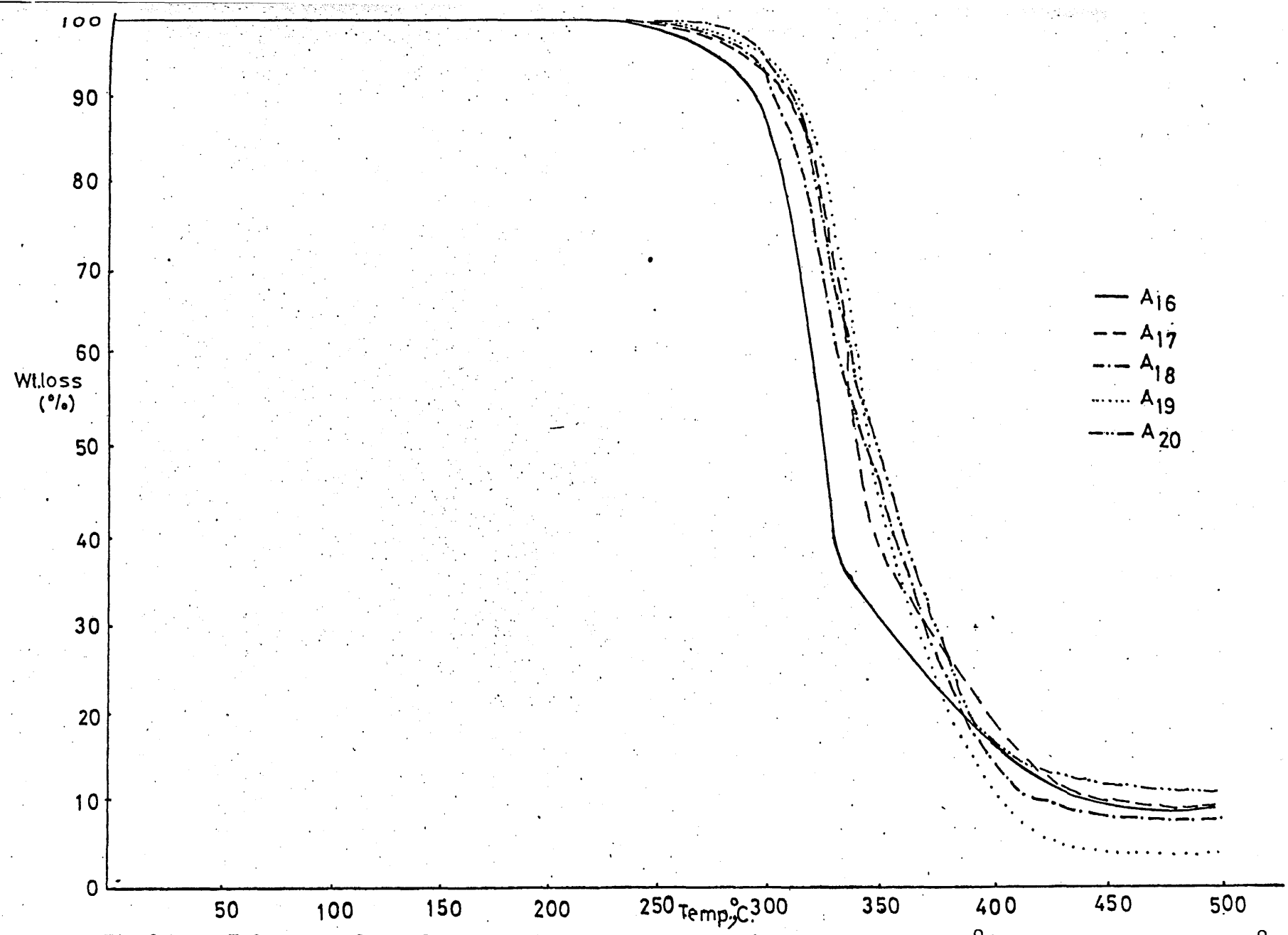


Fig.6.18. T G curves for 2,3 - D B P A - S copolymers (Samples heated at 10°/min from ambient to 500°C).

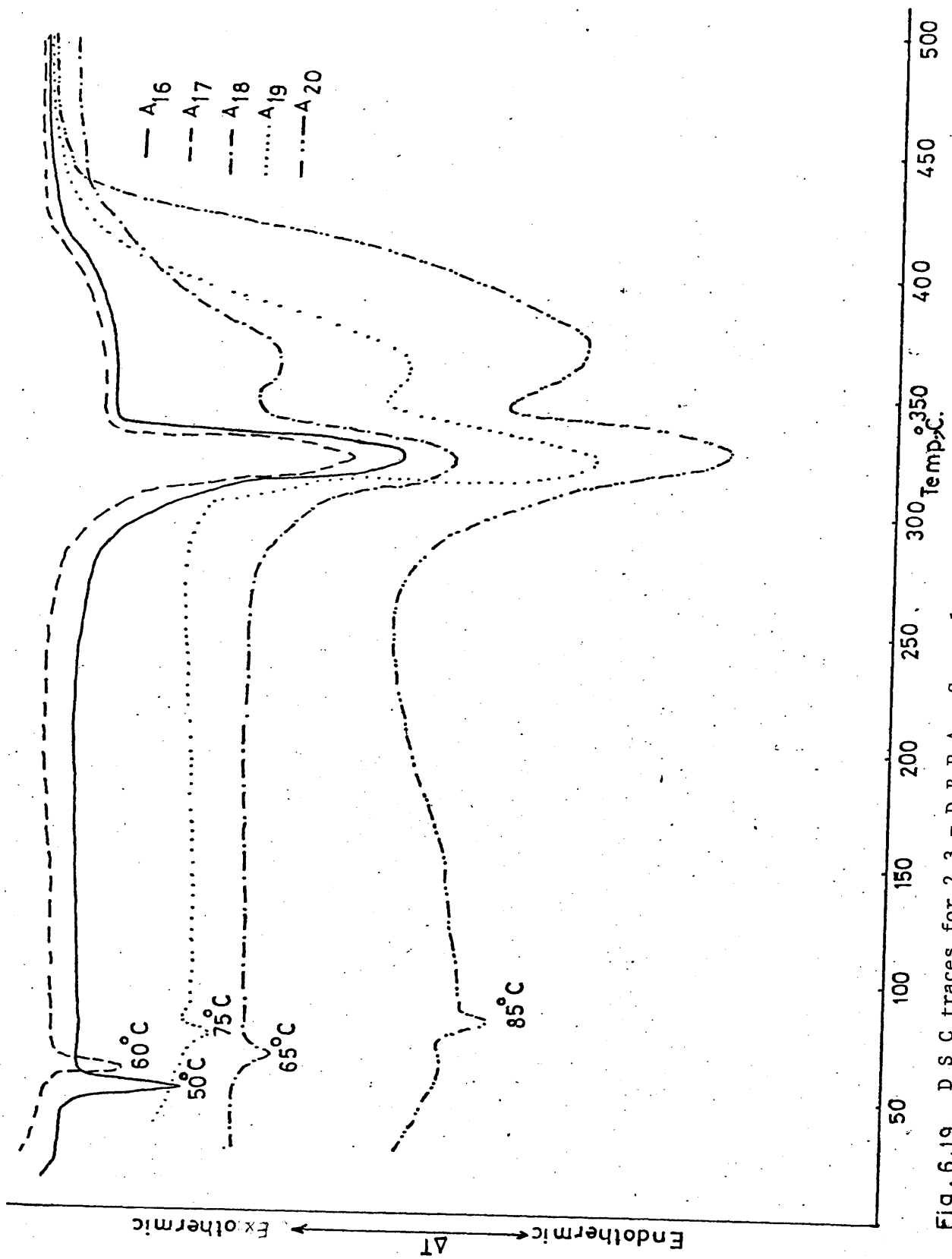


Fig. 6.19. D S C traces for 2,3 - D B P A - S copolymers.

temperature peak. The glass transition temperatures, T_g, of the copolymers range from 50°C to 85°C, decreasing as 2,3 - D B P A content increases.

iv. Subambient T V A and Product Analysis

The condensable degradation products were separated by subambient T V A using 50 mg samples of each of copolymer, which were heated from ambient temperature to 500°C at 10°C/min under normal T V A conditions.

Figure 6.20 shows the S A T V A trace of copolymer A_{18}, which exhibits four distinct peaks. I r, mass spectrometry and g l c were used to identify these products. Figure 6.21 shows the g l c trace for peaks 3 and 4, while peak 1 contains HBr, CO_2 and peak 2 contains allyl bromide. A list of the products of degradation is given in Table 6. 7. Again the products indicated by * should be regarded as tentative.

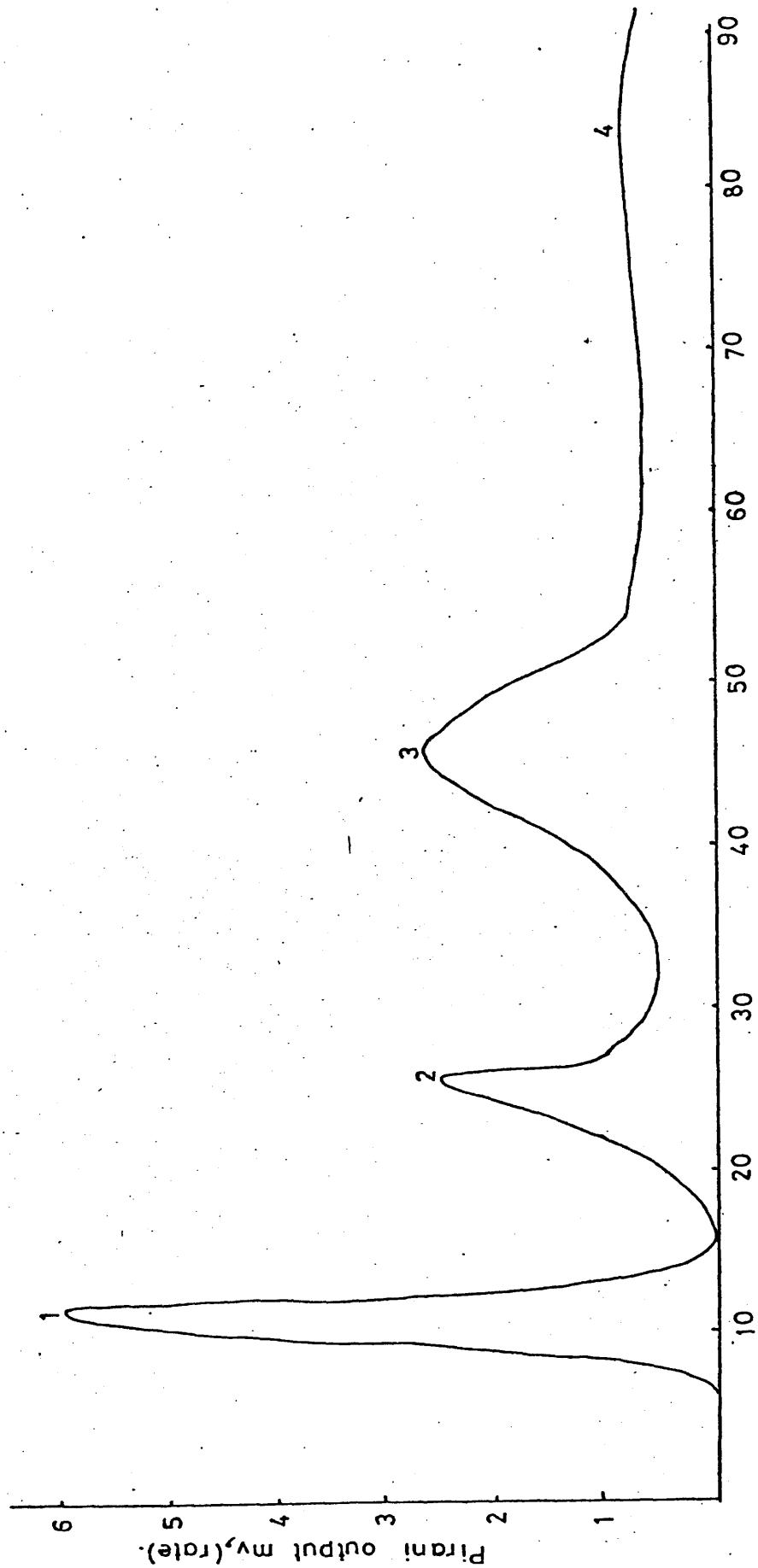
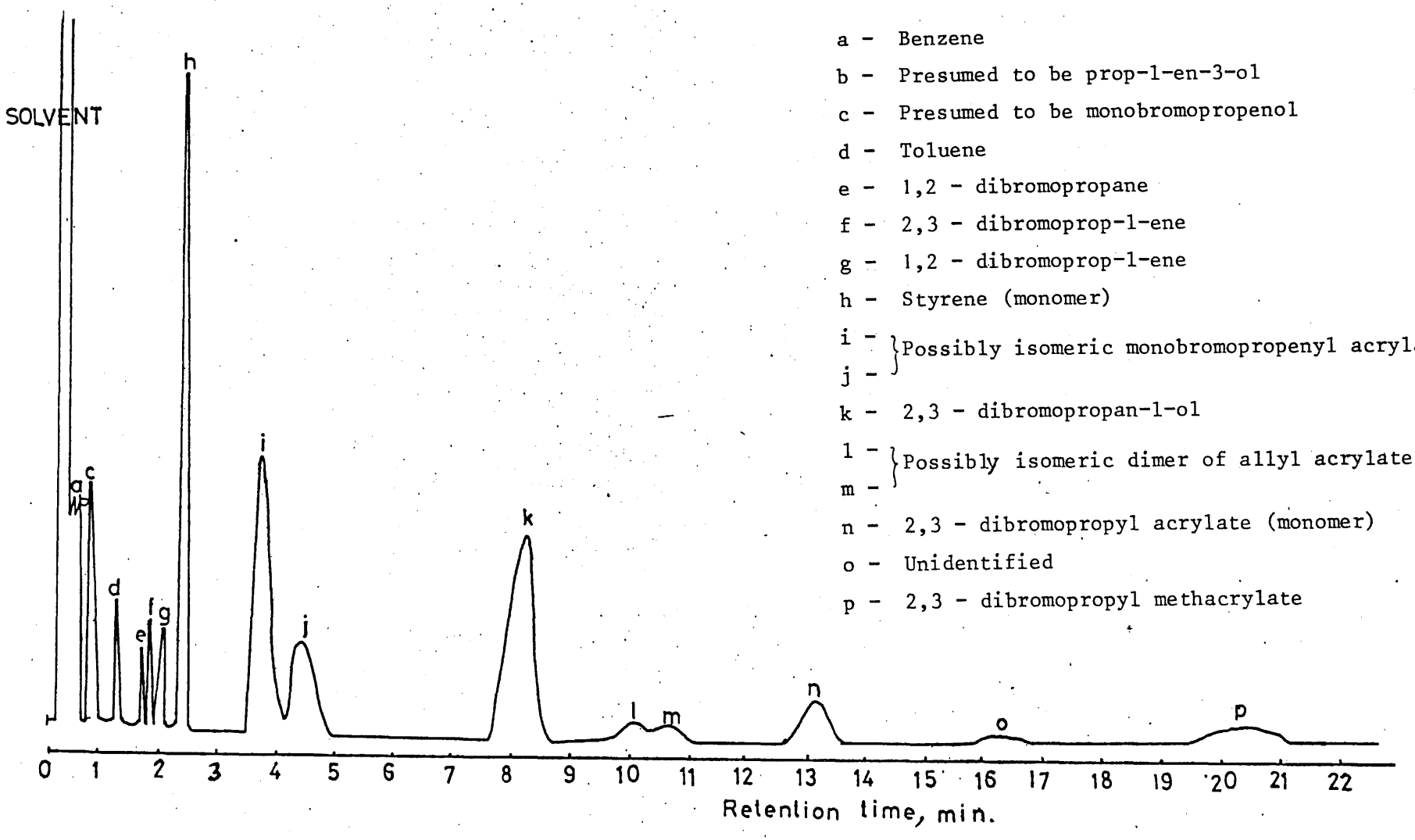


Fig. 6.20. S A T V A trace for the degradation products of 2,3 - D B P A - S copolymer (A_{18}), from programmed degradation under vacuum to 500°C at 10°/min , 50 mg sample.



a - Benzene
b - Presumed to be prop-1-en-3-ol
c - Presumed to be monobromopropenol
d - Toluene
e - 1,2 - dibromopropane
f - 2,3 - dibromoprop-1-ene
g - 1,2 - dibromoprop-1-ene
h - Styrene (monomer)
i - } Possibly isomeric monobromopropenyl acrylates
j - }
k - 2,3 - dibromopropan-1-ol
l - } Possibly isomeric dimer of allyl acrylate type
m - }
n - 2,3 - dibromopropyl acrylate (monomer)
o - Unidentified
p - 2,3 - dibromopropyl methacrylate

Fig. 6.21 . G L C trace for the degradation products of peaks 3 and 4 in the subambient T V A curve (figure 6.20) using 5 ft. $\frac{1}{4}$ inch diameter, 10% microwax on chromosorb column isothermally at 140°C.

Table 6. 7. Degradation products of 2,3 - D B P A - S Copolymer A_{18} from ambient temperature to 500°C at 10°/min

Degradation fraction	Products	Method of Analysis
Non-condensable materials	CH_4 , CO and H_2	I R & mass spectra
C R F	Long chain fragment of 2,3 - D B P A + dimer	
	trimer, tetramer, pentamer of styrene	I R in solution & g l c
Residue	Carbon	I R (K Br disc)
Condensable materials:		
Peak 1 (S A T V A)	CO_2 , HBr	I R & M S
Peak 2 (S A T V A)	Allyl bromide	I R & M S
Peak 3 (S A T V A)	Benzene, prop-1-en-3-ol*, monobromo propenol*, toluene, 1,2 - dibromopropane, 2,3 - dibromoprop-1-ene, 1,2 - dibromoprop-1-ene, styrene (monomer) and isomeric monobromopropenyl acrylate *	M S & g l c
Peak 4 (S A T V A)	2,3 - dibromopropan-1-ol, Isomeric dimeric species based on allyl acrylate*, 2,3 - dibromopropyl acrylate (monomer) and 2,3 - dibromopropyl methacrylate.	M S & g l c

The stepwise degradation procedure, described in Chapter 4, was carried out on a single sample of A_{18} copolymer in the S A T V A apparatus. The temperature of the stages ranged from 250° to 500°C. The series of S A T V A curves shown in Figure 6.22 was obtained. Again, HBr first appeared (peak 1) at a much higher temperature than the other three peaks.

v. Quantitative Measurement of Degradation Products

Infra-red spectroscopy was used for quantitative analysis of peaks 1 and 2 in the S A T V A and g l c for peaks 3 and 4. Table 6. 8 gives the quantitative analysis of the degradation products of 2,3 - D B P A - S copolymers heated to 500°C at 10°C/min. Values marked * should be regarded as tentative.

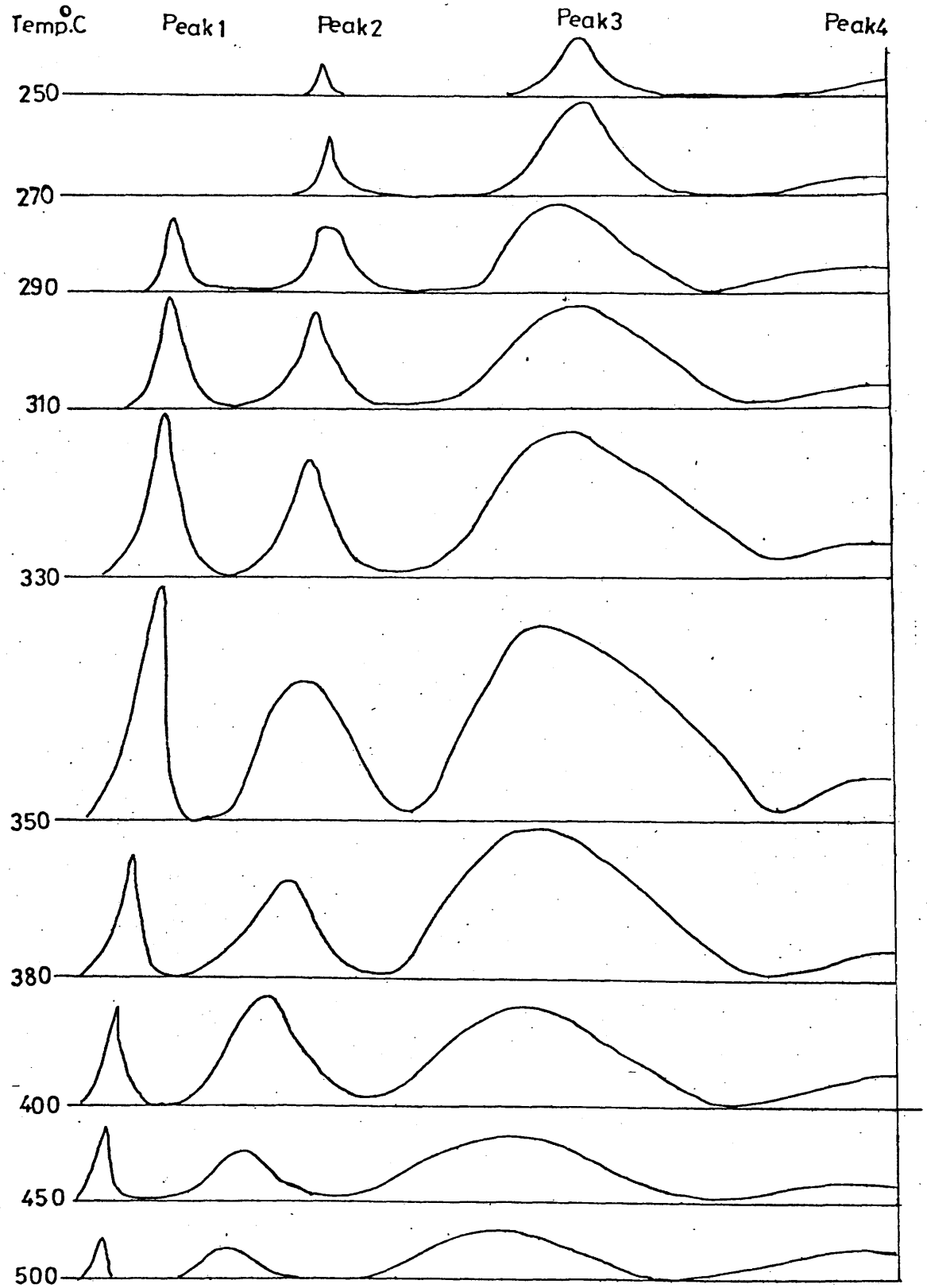


Fig. 6.22. Subambient T V A curves for degradation products of a single sample of 2,3 - D B P A - S copolymer (A_{18}) from programmed degradation under vacuum from ambient to successively higher temperatures at 10°/min , 50 mg sample size. Sample held at each temperature while products were collected for S A T V A.

Table 6. 8. Quantitative analysis of the products of degradation of 2,3 - D B P A - S Copolymers (20^{o}- 500^{o}C, at 10^{o}C/min)

Product	A_{16}	A_{17}	A_{18}	A_{19}	A_{20}
	Wt.(%)				
HBr	27.61	23.17	14.07	10.12	7.78
CO_2	4.5	3.8	2.1	1.5	1.2
Propene	0.5	0.5	0.4	0.4	0.4
Allyl bromide	5.00	4.3	2.2	1.9	1.3
Benzene	trace	trace	trace	trace	trace
Prop 1-en-3-ol	0.4*	0.3*	0.2*	0.2*	0.1*
Monobromoprop-1-en-3-ol	0.4*	0.3*	0.2*	0.1*	0.1*
Toluene	trace	trace	trace	trace	trace
1,2 - dibromopropane	1.6	1.3	0.7	0.5	0.3
2,3 - dibromoprop-1-ene	1.9	1.6	0.8	0.6	0.5
1,2 - dibromoprop-1-ene	2.1	1.7	0.8	0.6	0.5
Styrene (monomer)	16.3	21.2	28.6	32.2	34.2
Isomeric monobromopropenyl acrylates	1.9*	1.6*	0.9*	0.7*	0.7*
2,3 - dibromopropan-1-ol	2.2	2.0	1.7	1.0	0.9
Isomeric dimeric species based on allyl acrylates	0.8*	0.6*	0.4*	0.6*	0.8*
2,3 - dibromopropyl acrylate (monomer)	0.7	0.8	0.9	1.2	1.5
2,3 - dibromopropyl methacrylate	trace	trace	trace	trace	trace
C R F	26.5	29.0	38.0	42.0	45.0
Residue	5	5	4	4	3.5
Total product	97.41	97.17	95.97	97.62	98.78

6. 4 DISCUSSION

The thermal degradation of polystyrene has received a great deal of attention, and yet the mechanism of degradation is still the subject of controversy. However, the nature of the volatile products has led to general agreement on a number of points. The mechanism of degradation usually proposed involves both intra and inter-molecular transfer reactions in addition to a simple depolymerisation reaction[44,45,46,47], but the ways in which these various reactions are initiated have, as yet, not been resolved completely.

Jellinek[48] first proposed that "weak links" are present, and this idea was more thoroughly investigated by Grassie and Kerr[49,50] and Cameron and Grassie[51,52,53]. Although these authors did obtain evidence to suggest that "weak links" might be associated with unsaturated structures, Cameron and Kerr[54] have suggested that the "weak links" arise from oxygenated groups, probably peroxide links, which have become incorporated into the polymer chain during polymerisation. Grassie and Farish[55] have studied the thermal degradation behaviour of M M A - S copolymers, and the degradation products consisted mainly of both monomers. Sequences of at least ten styrene units were necessary for the production of styrene dimer, trimer and tetramer. In a recent study Zhubanov and co-workers[56] examined the possibility that the incorporation of V B units into the polymer chain of polystyrene might confer flame retardance. Hrabak et al[57], studied the thermal degradation of copolymers of Styrene and some chlorinated methacrylates and acrylates, and they found that some interaction may occur between the comonomer units to produce minor products such as chlorobenzene and chlorotoluene. In the thermal degradation of

2,3 - D B P M - S and 2,3 - D B P A - S copolymers, there is no evidence of interaction leading to products of this kind. From the weight loss and volatilisation information it is evident that the 2,3 - D B P M - S and 2,3 - D B P A - S copolymer systems have an intermediate stability with respect to the respective homopolymers. It is clear from the results given in Table 6. 4 that the degradation products of the 2,3 - D B P M - S copolymers are primarily the two monomers, together with the other products formed in the degradation of P2,3 - D B P M and polystyrene homopolymers. The relative amounts of the monomers reflect the changing copolymer composition. Similar observations can be made about the degradation products of 2,3 - D B P A - S copolymers, with the exception that the formation of 2,3 - D B P A monomer increases as the 2,3 - D B P A content of the copolymer decreases. This is consistent with a similar effect observed in the degradation of 2,3 - D B P A - M M A copolymers described in Chapter 5 and the same explanation seems adequate. The large proportion of cold ring fraction obtained in the degradation of 2,3 - D B P M - S and 2,3 - D B P A - S copolymers is expected, simply reflecting the general characteristics of degradation of polystyrene. This gives about 42% monomer , and the remaining degradation products are oligmers which can appear as a cold ring fraction. The amount of cold ring fraction increases as the styrene content of the copolymers increases, which supports the above view.

CHAPTER 7

THERMAL DEGRADATION of 2,3 - D B P M - M A and 2,3 - D B P A - M A COPOLYMERS

7. 1 INTRODUCTION

The thermal degradation of P M A was first studied by Straus and Madorsky[58]. They found that the main product of degradation (73% by weight) was a low polymer fraction with an average molecular weight of 633. Other volatile products identified were methanol (15%), carbon dioxide (7.5%), methyl acrylate (0.7%), methyl methacrylate (0.1%) and C_4 - C_6 oxygenated compounds (3.9%). Madorsky[59] concluded that the mechanism of the thermal degradation could be explained by disproportionation reactions. Quite small concentrations of copolymerised acrylate can act as a very effective stabiliser for P M M A[40]. In this chapter the thermal degradation behaviours of 2,3 - D B P M - M A and 2,3 - D B P A - M A copolymers will be discussed, and their degradation products reported either qualitatively or quantitatively. Finally, mechanisms of degradation consistent with the stabilities of the copolymers will be proposed.

7. 2 THERMAL DEGRADATION of 2,3 - D B P M - M A COPOLYMERS

i. Molecular Weights

Number Average Molecular Weights were measured using a Mechrolab high-speed membrane osmometer as described in Chapter 2. Five copolymers of 2,3 - D B P M - M A were prepared by the method outlined in Chapter 2, and their composition determined by the microanalysis and n m r spectroscopic techniques, described in Chapter 3. Copolymers were prepared with 83% (A_{21}), 70% (A_{22}),

51% (A_{23}), 28% (A_{24}) and 18% (A_{25}) of methacrylate monomer. The Number Average Molecular Weights of these copolymers are listed in Table 7. 1. It was observed that as the M A content increased, the polymer became softer and more tacky and consequently more difficult to handle. Copolymers A_{21}, A_{22} and A_{23} were powders; copolymers A_{24} and A_{25} were soft and tacky. For thermal analysis, copolymers A_{24} and A_{25} were cut into very small pieces to simulate a powder.

Table 7. 1. Number Average Molecular Weights of 2,3 - D B P M - M A Copolymers

Polymer	$\overline{M}_n$
A_{21}	444,000
A_{22}	345,000
A_{23}	164,000
A_{24}	152,000
A_{25}	136,000

ii. Thermal Volatilisation Analysis (T V A)

The T V A traces of copolymers A_{21}, A_{22}, A_{23}, A_{24} and A_{25} are shown in figures 7. 1, 7.2, 7.3, 7. 4 and 7.5 respectively. There are two distinct peaks; the second peak becomes more important at higher concentrations of M A in the copolymer. Volatilisation starts at 246°C and reaches maxima at 330°C and 391°C. All the traces are separated to some extent in each peak, suggesting that products with a range of volatilities are being evolved, in addition to a non-condensable fraction. Also, cold ring fractions coloured

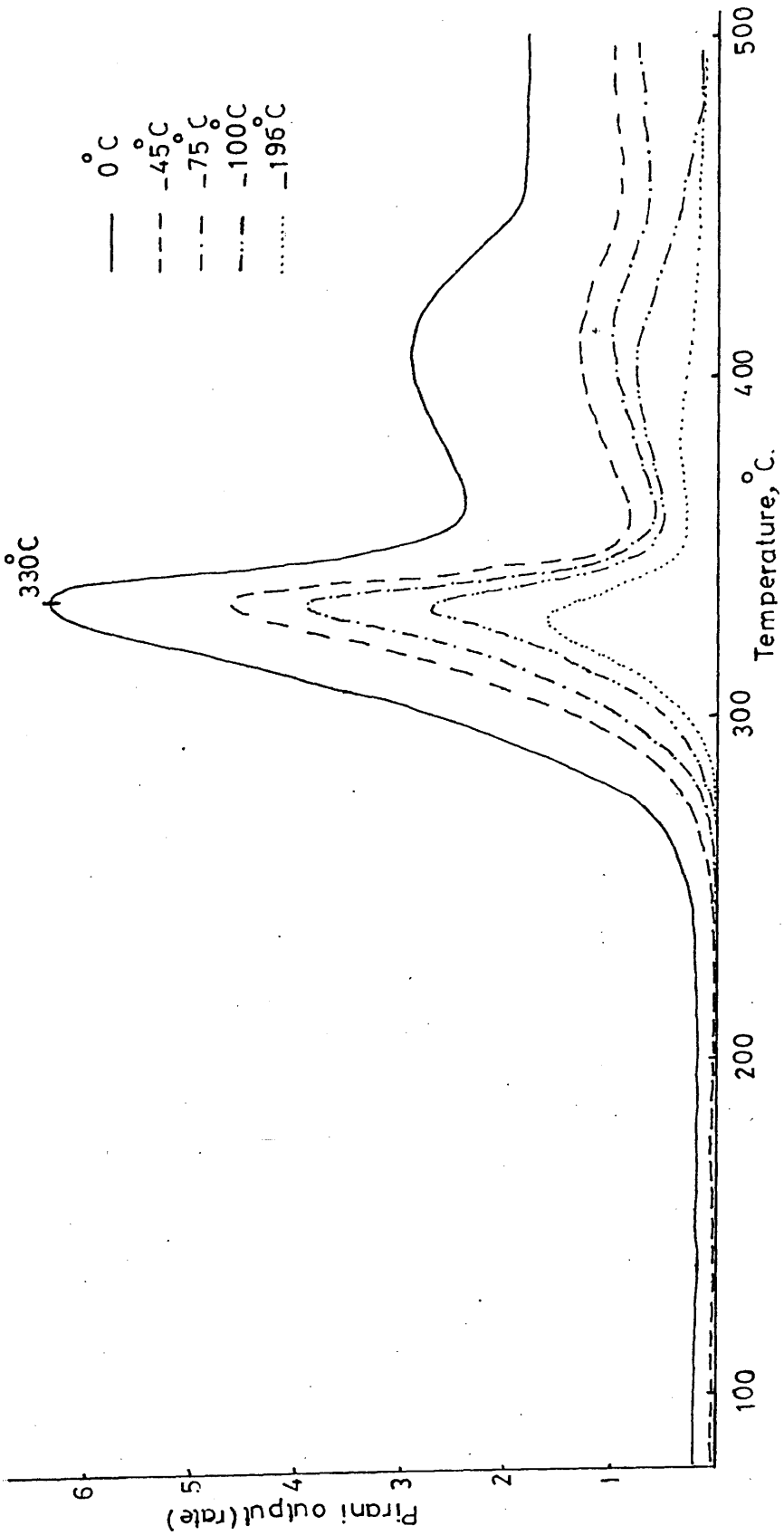


Fig. 7.1. T V A thermogram for A_{21} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

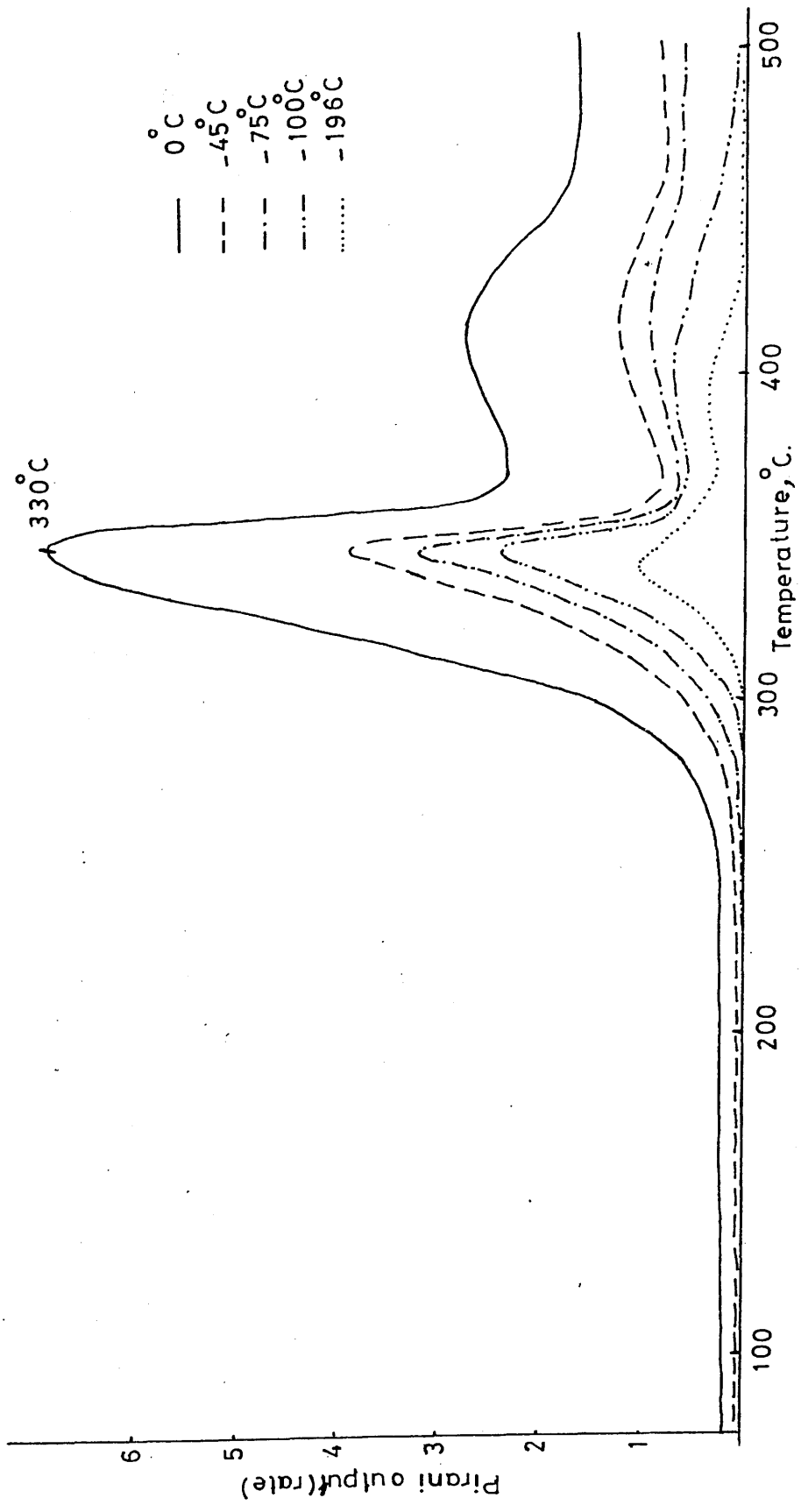


Fig.7.2. T V A thermogram for A_{22} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

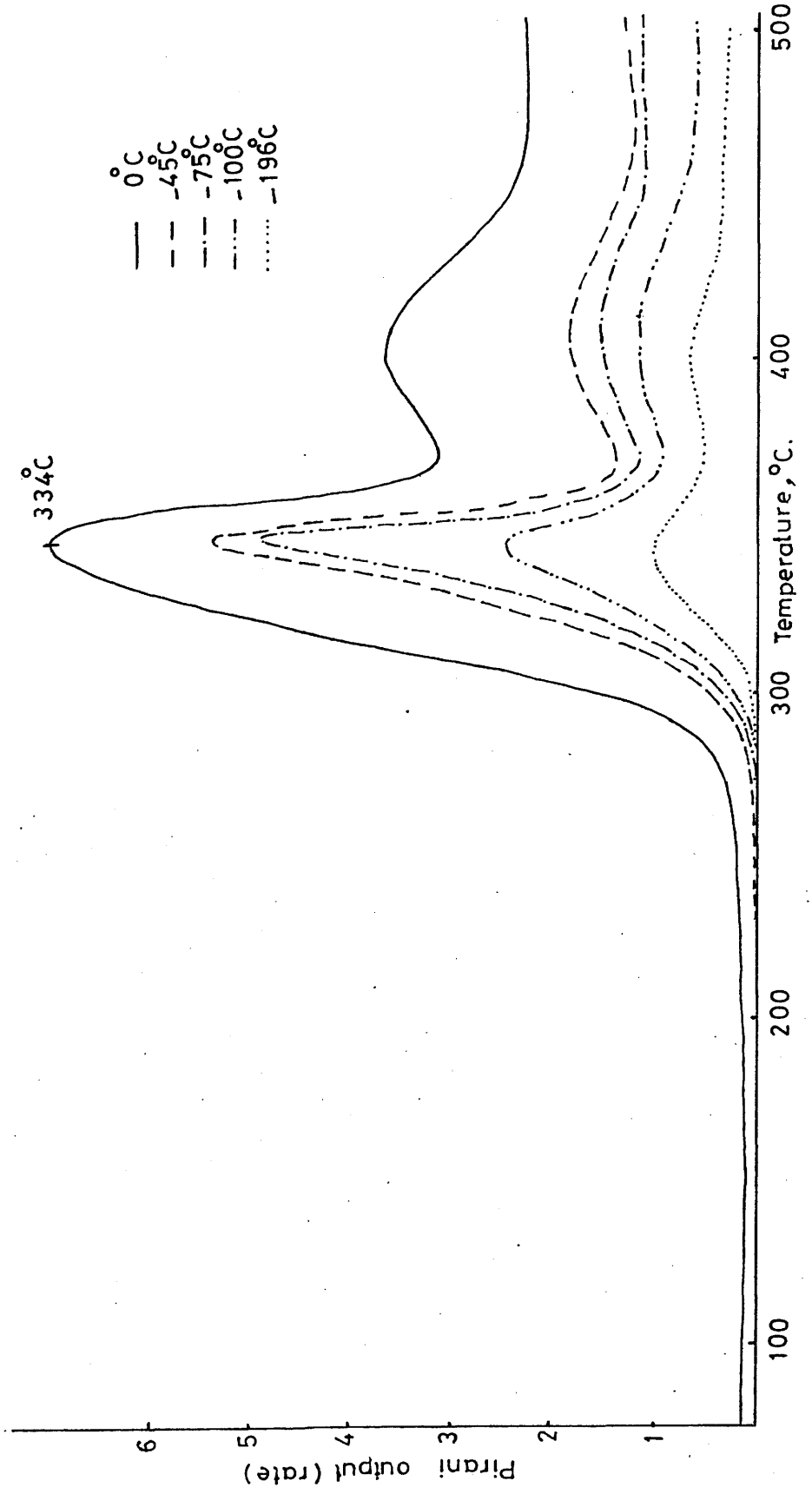


Fig. 7.3. T V A thermogram for A_{23} copolymer, sample size 50mg ; heating rate 10^{o}/min.

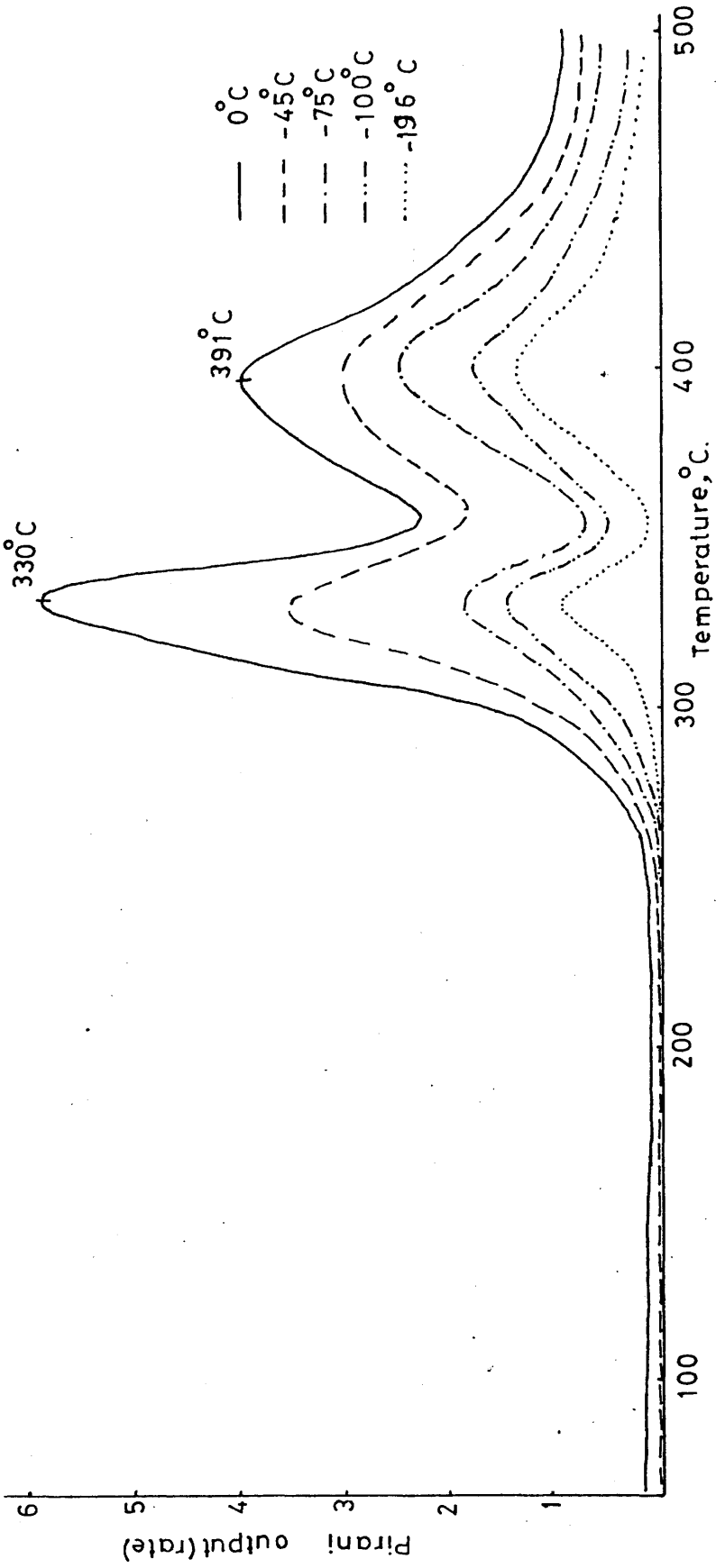


Fig. 7.4. T V A thermogram for A_{24} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

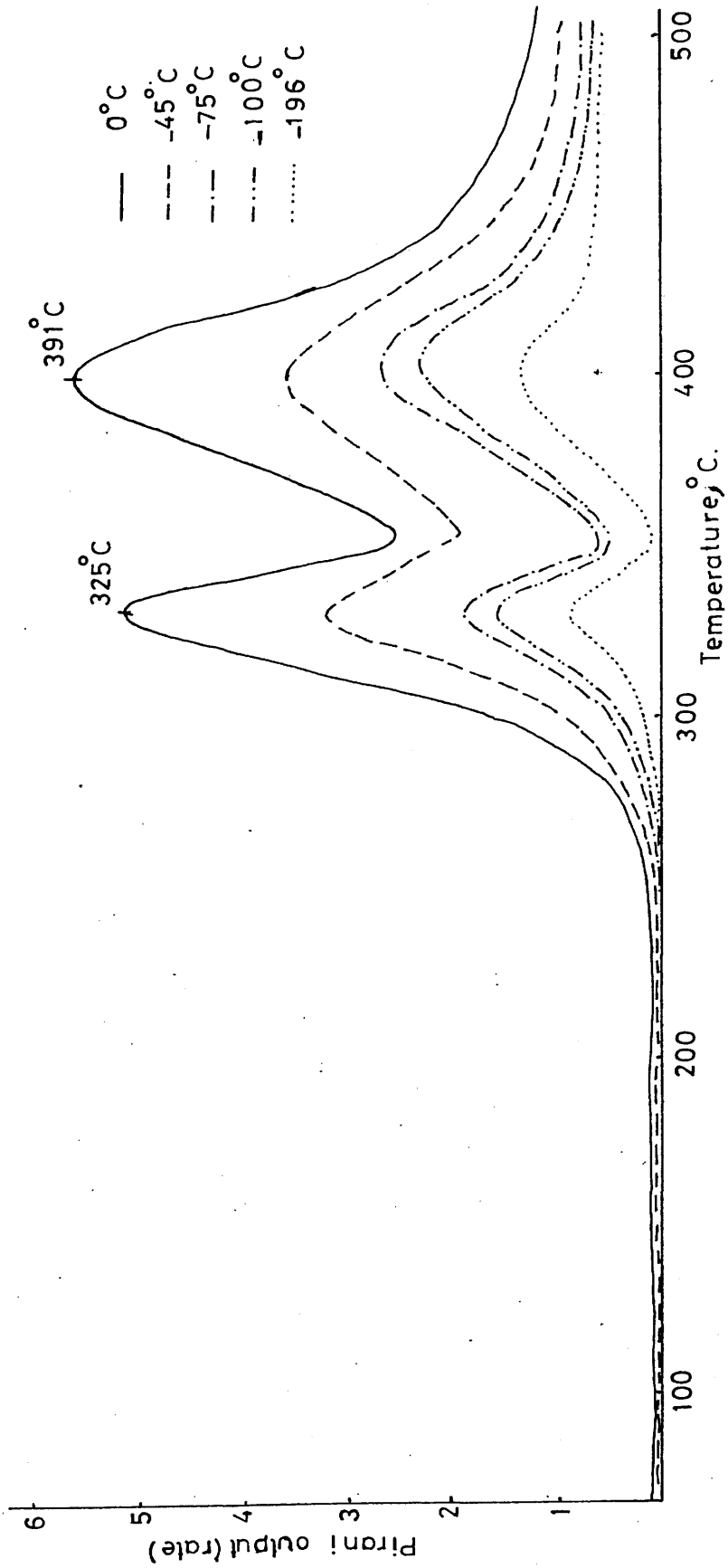


Fig. 7.5. T V A thermogram for A_{25} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

deep yellow are formed in each case, and small amounts of residue remain.

iii. T G and D S C

T G curves for 2,3 - D B P M - M A copolymers are illustrated in figure 7.6. The weight loss curves obtained under nitrogen have two distinct stages, the relative importance of each stage being dependant on the copolymer composition. Table 7. 2. shows the percentage weight loss of each copolymer in each stage. The weight loss starts at 250°C, and copolymer A_{25} is more stable than the other copolymers.

Table 7. 2. Percentage weight loss for 2,3 - D B P M - M A copolymers

Polymer	First stage		Second stage		% of weight remaining at 500°C
	T_{max}, °C	Weight loss (%)	T_{max}, °C	Weight loss (%)	
P2,3 - D B P M	325	84	400	4	12
A_{21}	330	78	390	10	12
A_{22}	340	75	395	15	10
A_{23}	335	72	390	18	10
A_{24}	330	42	400	46	12
A_{25}	340	36	410	52	12
PM A	415	95	-	-	5

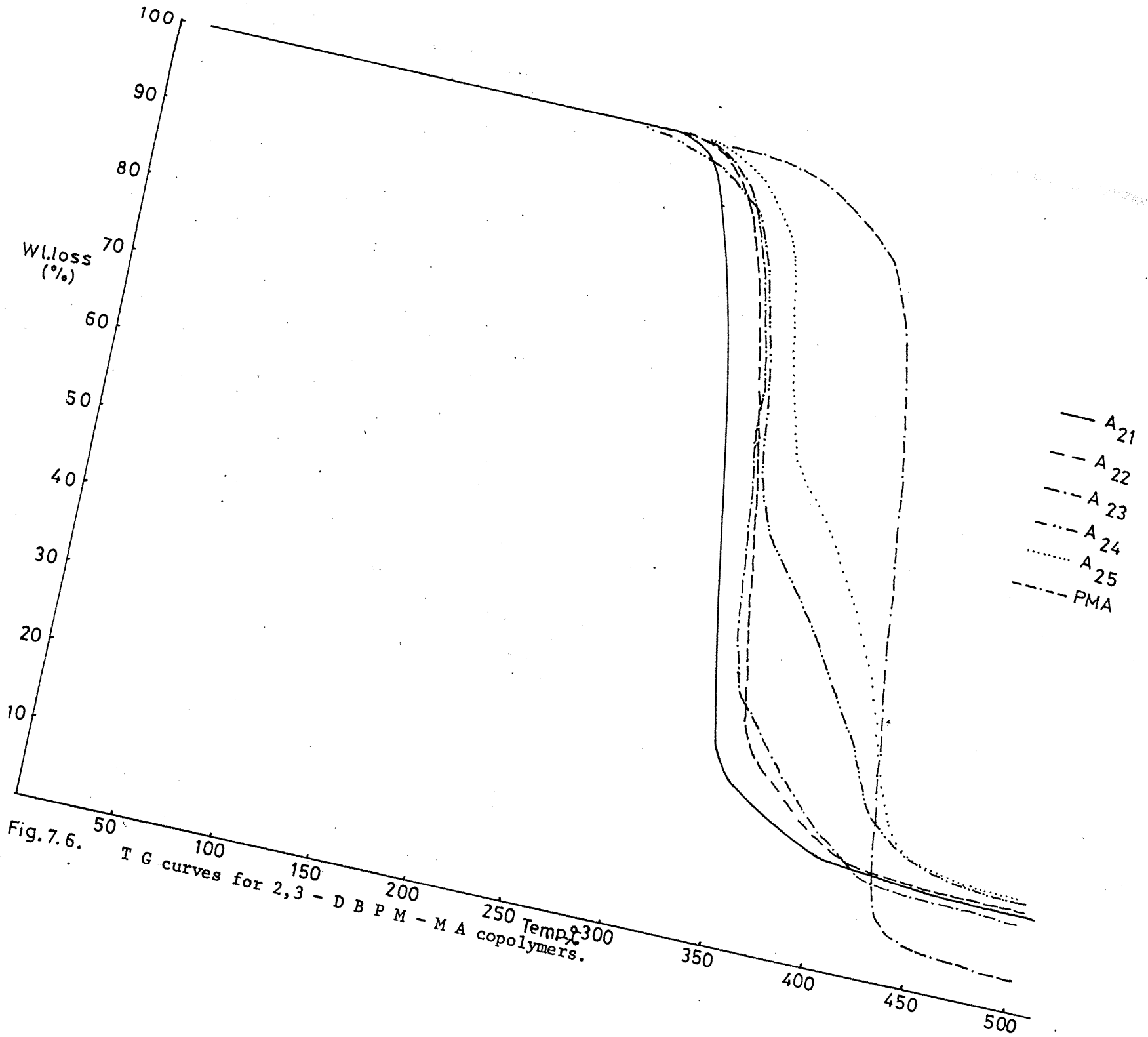


Fig. 7.6. T G curves for 2,3 - D B P M - M A copolymers.

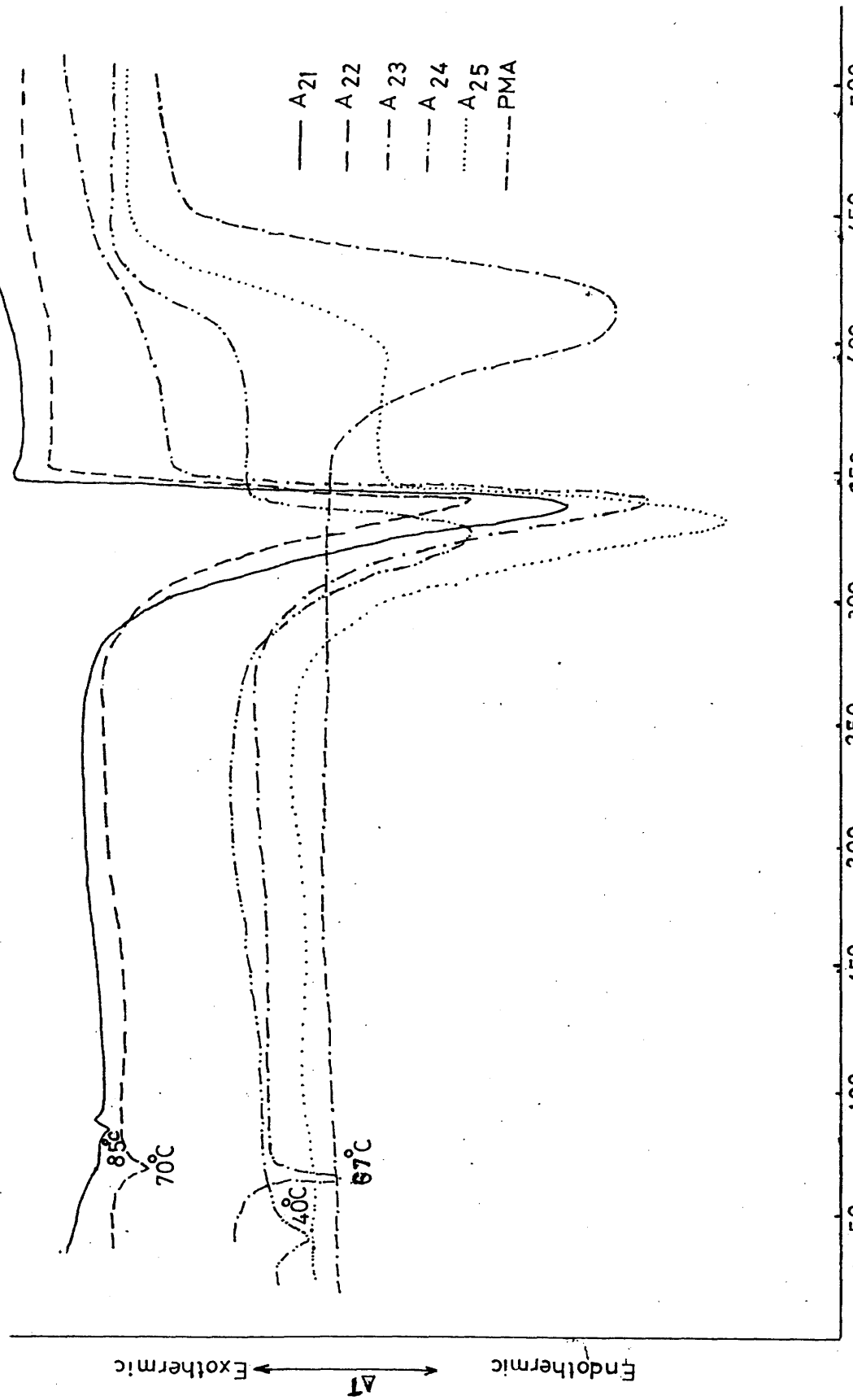


Fig. 7.7. D S C curves for 2,3 - D B P M - M A copolymers.

D S C curves for the five copolymers displaying two endothermic peaks are illustrated in figure 7.7. T_g values range from 85°C to 40°C, decreasing as the M A content of the copolymer increases.

iv. Subambient T V A and Product Analysis

The degradation products of the 2,3 - D B P M - M A copolymers may be separated into fractions as follows.

a. The non-condensable materials may be collected in a closed system as described in Chapter 2 and their i r spectrum reveals carbon monoxide, methane and propene. Hydrogen is detected from the mass spectrum.

b. Infra-red spectroscopy indicates that the cold ring fraction contains polymethacrylic anhydride structures and chain fragments containing methyl acrylate.

c. The residue left on the base of the degradation tube is a black carbonaceous char with no well developed absorptions in the i r.

d. Condensable products were separated by subambient T V A as shown in figure 7.8. There are seven distinct peaks. I r spectroscopy and mass spectrometry were used to identify peaks 1, 2 and 3, while g l c and mass spectrometry were employed for peaks 4, 5, 6 and 7. The results are shown in figures 7.9 and 7.10. A complete list of the products of degradation of the 2,3 - D B P M - M A copolymers is shown in Table 7. 3. The products indicated by * have been inferred from mass spectral data in the absence of reference compounds.

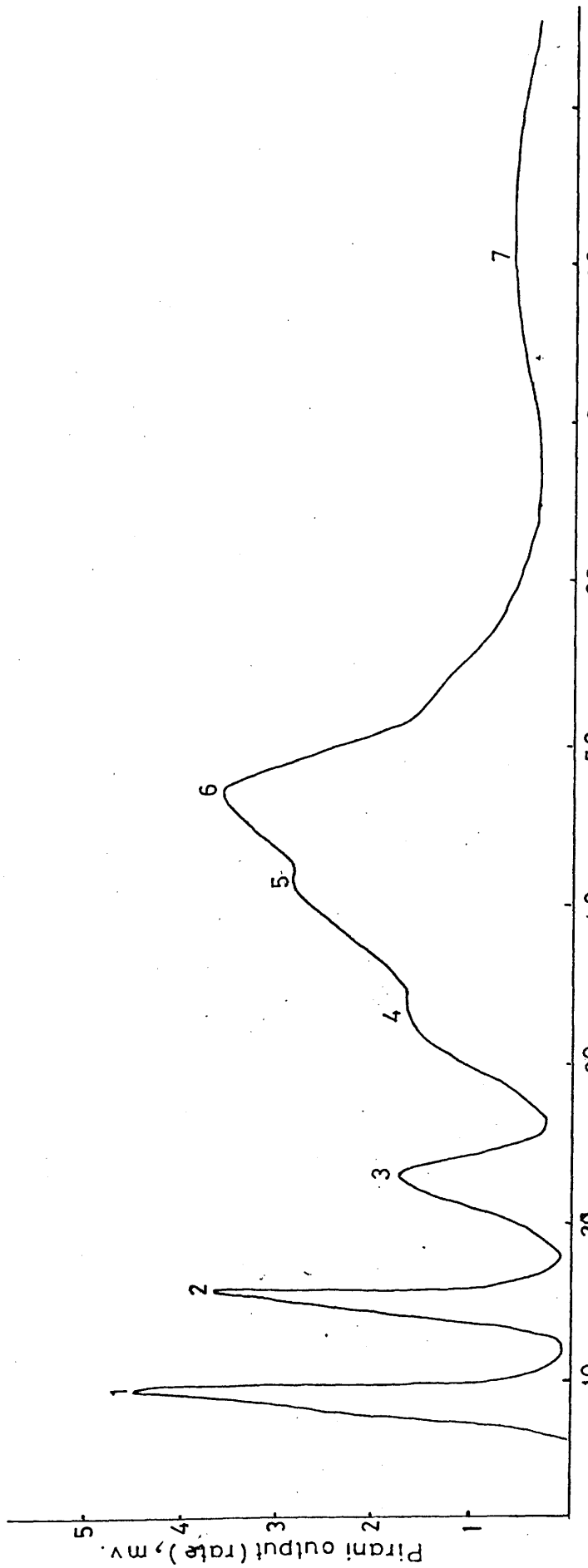


Fig. 7.8. Subambient T V A trace for degradation products of 2,3 - D B P M - M A copolymer (A_{23}) from programmed degradation under vacuum to 500°C at 10°/min , 50 mg sample.

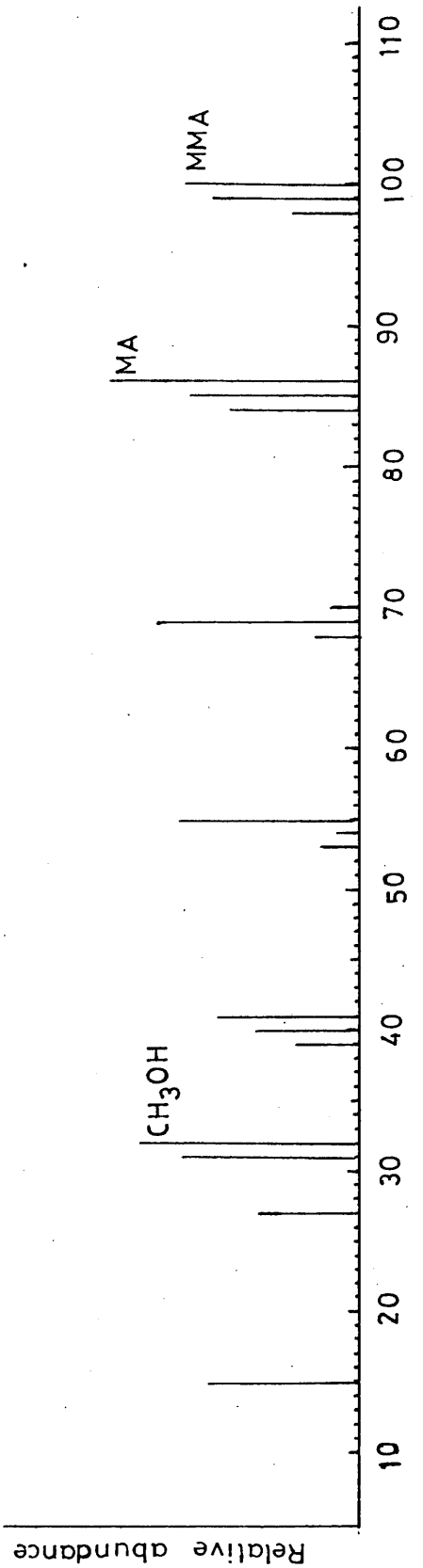
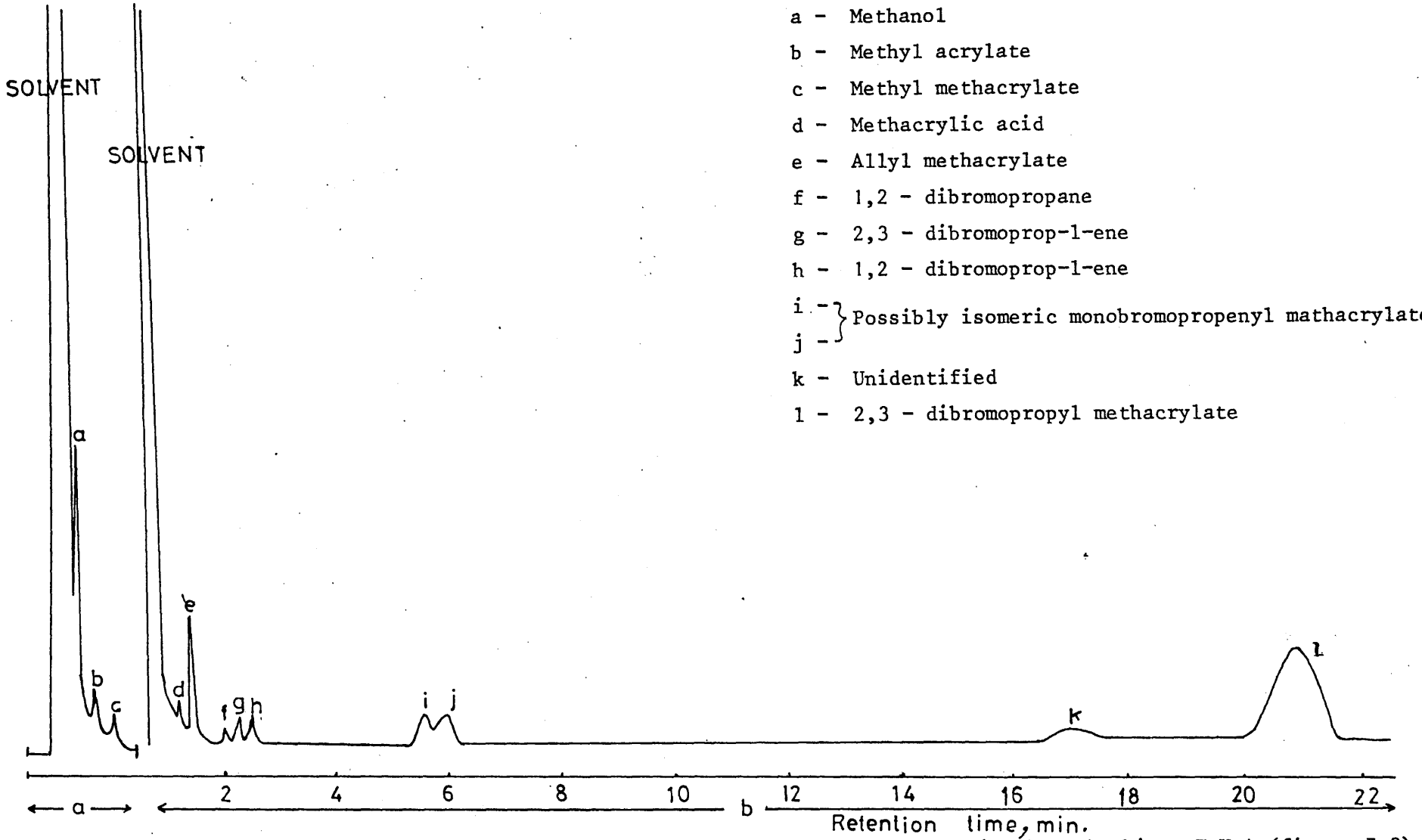


Fig. 7.9. Mass spectrum of peaks 4, 5 in subambient T V A of 2,3 - D B P M - M A copolymer degradation.



a - Methanol
b - Methyl acrylate
c - Methyl methacrylate
d - Methacrylic acid
e - Allyl methacrylate
f - 1,2 - dibromopropane
g - 2,3 - dibromoprop-1-ene
h - 1,2 - dibromoprop-1-ene
i - } Possibly isomeric monobromopropenyl mathacrylate
j - }
k - Unidentified
l - 2,3 - dibromopropyl methacrylate

Fig. 7.10. G L C trace for the degradation products from peaks 4, 5, 6 and 7 in the subambient T V A (figure 7.8) using 5 ft. $\frac{1}{4}$ inch diameter, 10% microwax on chromosorb column isothermally at a) 90°C b) 140°C.

Table 7. 3. Degradation Products of 2,3 - D B P M - M A Copolymers

Degradation fraction	Products	Method of Analysis
Non-condensable materials	CH_4, CO , propene , H_2	I R & M S
Cold ring fraction	Polymethacrylic anhydride structures, chain fragments	I R in solution
Residue	Carbon	I R (K Br disc)
Condensable materials :		
Peak 1 (S A T V A)	CO_2 , HBr	I R & M S
Peak 2 (S A T V A)	CH_3 Br	I R & M S
Peak 3 (S A T V A)	Allyl bromide	I R & M S
Peak 4 (S A T V A)	Methanol	g l c & M S
Peak 5 (S A T V A)	Methyl acrylate (monomer), methyl methacrylate	g l c & M S
Peak 6 (S A T V A)	H_2O, Br_2, methacrylic acid, Allyl methacrylate, 1,2 - dibromopropane, Isomeric dibromopropenes, and Isomeric monobromopropenyl methacrylates *	
Peak 7 (S A T V A)	2,3 - dibromopropyl methacrylate (monomer)	g l c & M S

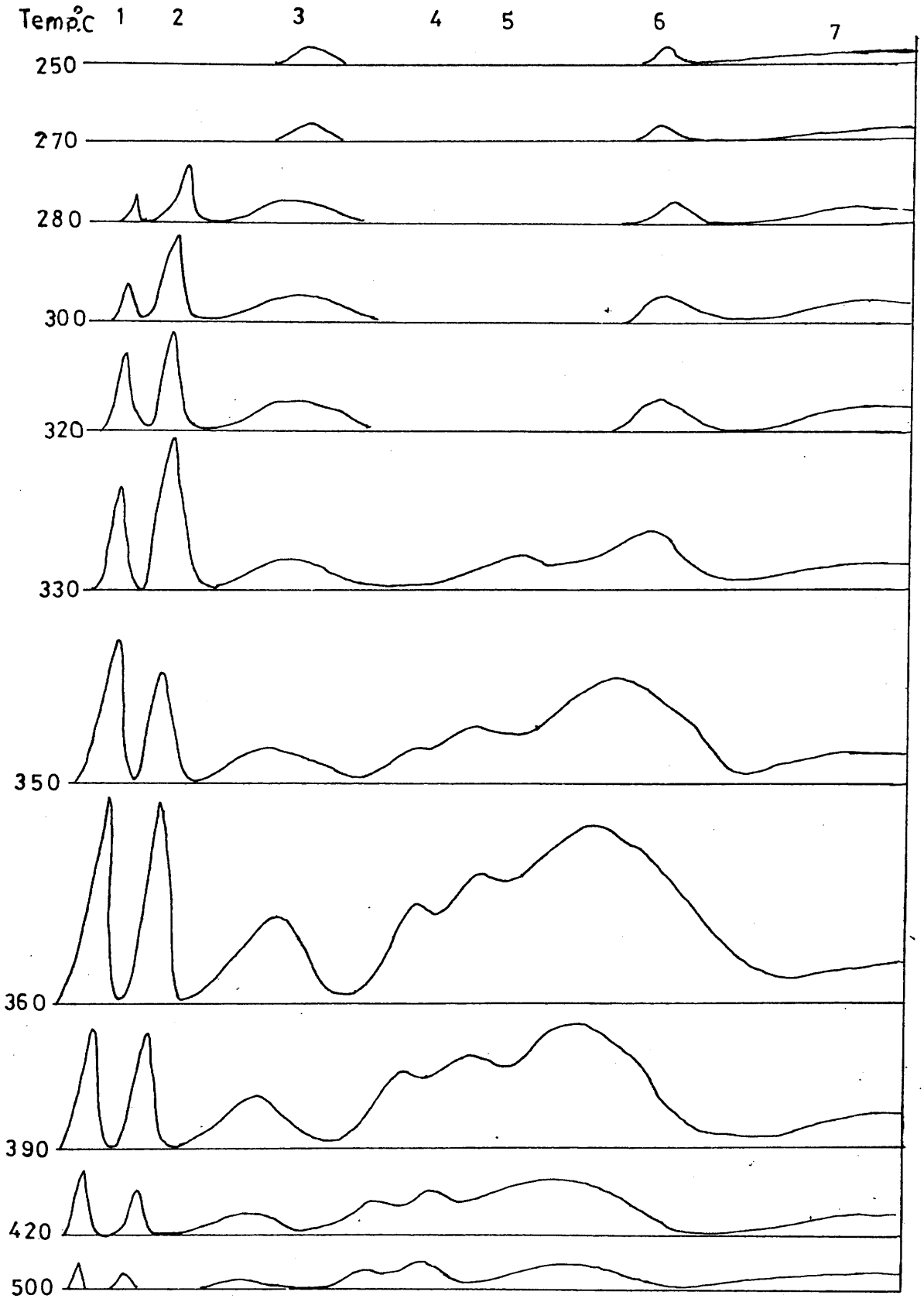


Fig.7.11. S A T V A curves for degradation of a single sample of A_{23} copolymer (from ambient temperature to successively higher temperture at 10^{o}/min , 50 mg sample size). Sample held at each temperature while products were collected for S A T V A.

The stepwise degradation procedure, as described previously was carried out on a single sample of (A_{23}) copolymer in the S A T V A apparatus, the temperatures of the stages ranging from 250°C to 500°C. The series of S A T V A curves obtained is shown in figure 7.11. The methyl bromide peak first appeared at 280°C, displaying two maxima at 330°C and 360°C. The methanol peak first appeared at 350°C and reached a maximum at 360°C. It seems that methanol production is associated with the second stage of degradation. Peaks 3, 5, 6 and 7 were present at all stages from 250°C.

v. Quantitative Measurement of the Degradation Products

Table 7. 4 presents the quantitative measurement of the degradation products of 2,3 - D B P M - M A copolymers, using infra-red spectroscopic techniques for peaks 1, 2 and 3 and g 1 c techniques for the products in peaks 4, 5, 6 and 7. The products indicated by * should not be regarded as being conclusively identified. Figure 7.12 represents the variation in amount of CH_3Br, CH_3OH and cold ring fraction with the molar composition of the copolymers after degradation to 500°C.

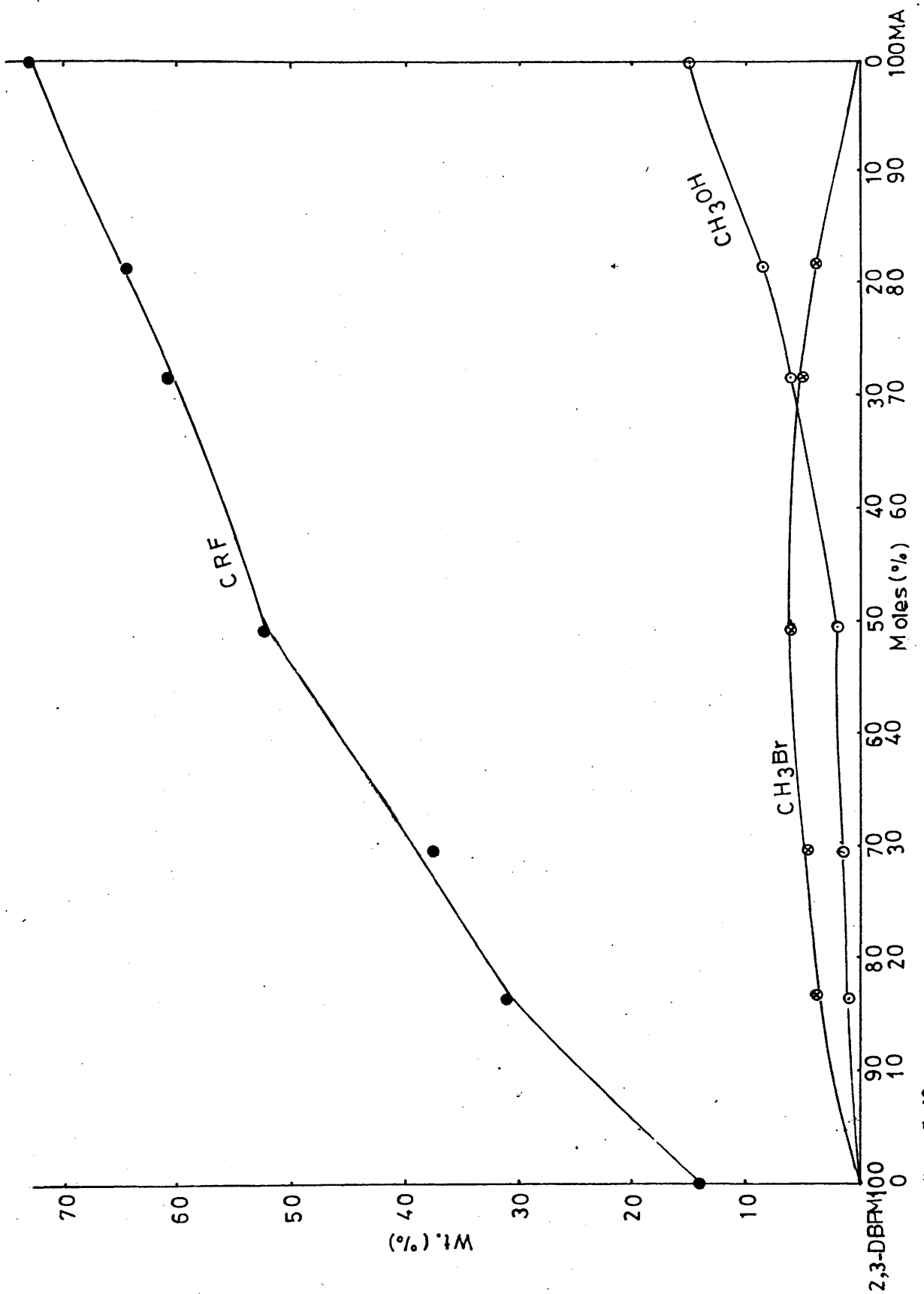


Fig.7.12. CH_3Br, CH_3OH and C R F versus copolymer composition.

Table 7. 4. Quantitative Analysis of the Degradation products of 2,3 - D B P M - M A Copolymers (20° - $500^{\circ}C$ at $10^{\circ}C$/min)

Products	A_{21}	A_{22}	A_{23}	A_{24}	A_{25}
	Wt.(%)				
HBr	3.9	1.6	0.6	trace	trace
CO_2	3.1	3.8	4.3	5.2	5.9
Propene	0.2	0.1	0.1	0.1	0.1
CH_3 Br	3.9	4.7	6.2	5.2	4.2
Allyl bromide	2.05	1.75	1.25	0.8	0.6
CH_3 OH	0.7	1.12	1.9	5.59	8.75
Methyl acrylate (monomer)	0.9	1.5	1.5	1.7	2.2
Methyl methacrylate	trace	trace	trace	trace	0.1
H_2O	trace	trace	trace	trace	trace
Br_2	2.1	1.9	1.2	0.7	0.4
Methacrylic acid	trace	trace	trace	trace	trace
Allyl methacrylate	2.0	1.5	1.0	0.5	0.3
1,2 - dibromopropane	0.2	0.1	0.1	trace	trace
Isomeric dibromopropenes	0.5	0.4	0.3	0.1	trace
Isomeric dibromopropenyl methacrylates *	1.2	0.7	0.4	0.3	0.1
2,3 - dibromopropyl methacrylate	40.3	37.0	25.1	15.6	8.8
Cold ring fraction	30.9	37.5	52.3	60.2	64.6
Residue	3	2	2	2	2
Total products	94.95	95.67	98.25	97.99	98.05

7. 3 THERMAL DEGRADATION of 2,3 - D B P A - M A COPOLYMERS

i. Molecular Weights

Five copolymers of 2,3 - D B P A - M A were prepared to 5% conversion by the method outlined in Chapter 2, their brominated monomer contents being 52% (A_{26}), 42% (A_{27}), 30% (A_{28}) 14% (A_{29}) and 9% (A_{30}). Table 7. 5 presents the Number Average Molecular Weights of these copolymers. It was observed that they were all soft and tacky and consequently difficult to handle. For thermal analysis they were cut into very small pieces to simulate a powder.

Table 7. 5. Number Average Molecular Weights of 2,3 - D B P A - M A Copolymers

Polymer	$\overline{M}_n$
A_{26}	248,000
A_{27}	189.000
A_{28}	118,000
A_{29}	112,000
A_{30}	73,000

ii. Thermal Volatilisation Analysis (T V A)

The T V A traces of the copolymers A_{26}, A_{27}, A_{28}, A_{29} and A_{30} are shown in figures 7. 13, 7. 14, 7. 15, 7. 16 and 7. 17 respectively. There are two distinct peaks in each case, the second peak becoming more important at higher concentrations of M A in the copolymer. Volatilisation starts at 240°C, reaches a maximum in the first stage between 319°C and 331°C, and in the second stage between 391°C

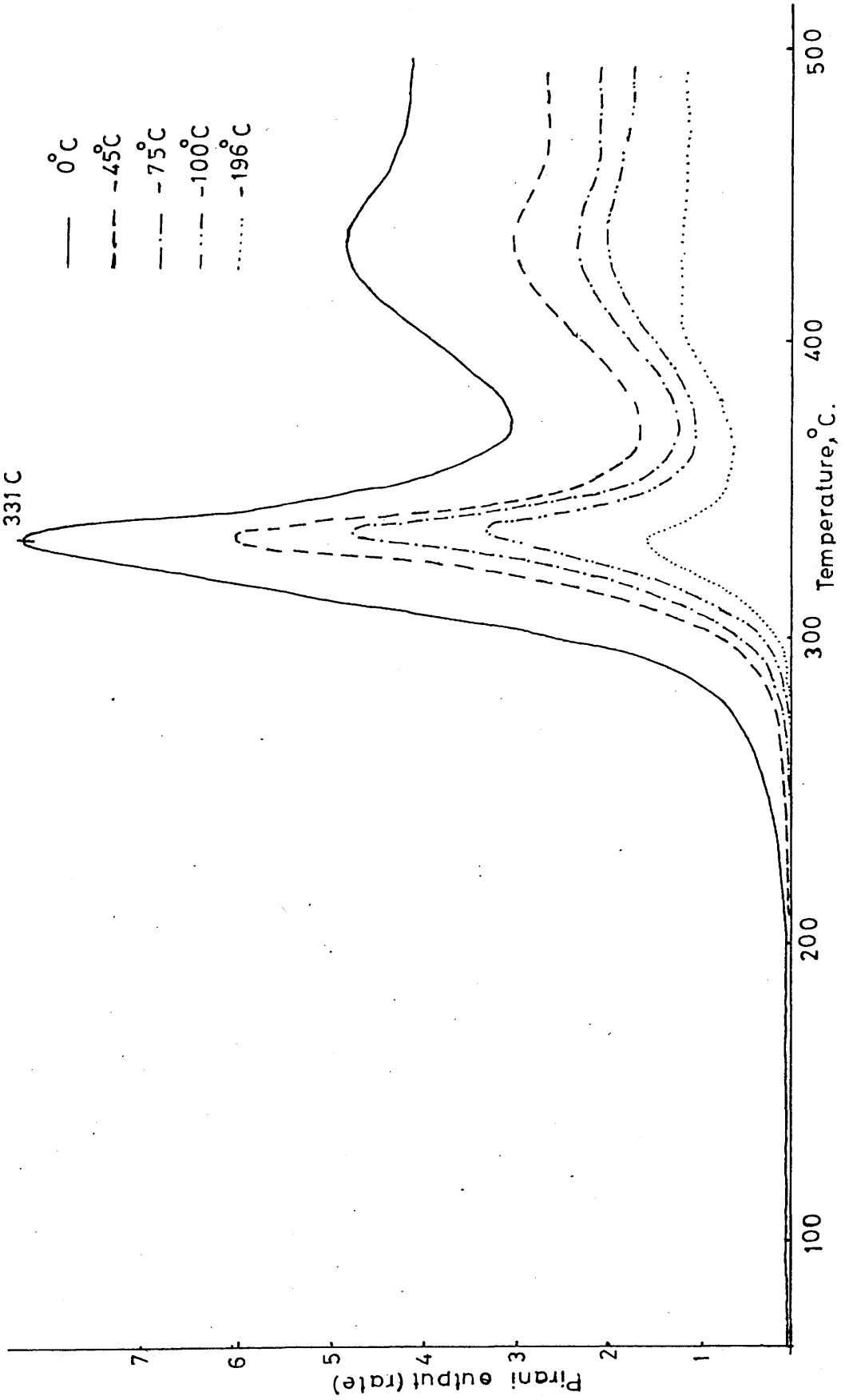


Fig. 7.13. T V A thermogram for A_{26} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

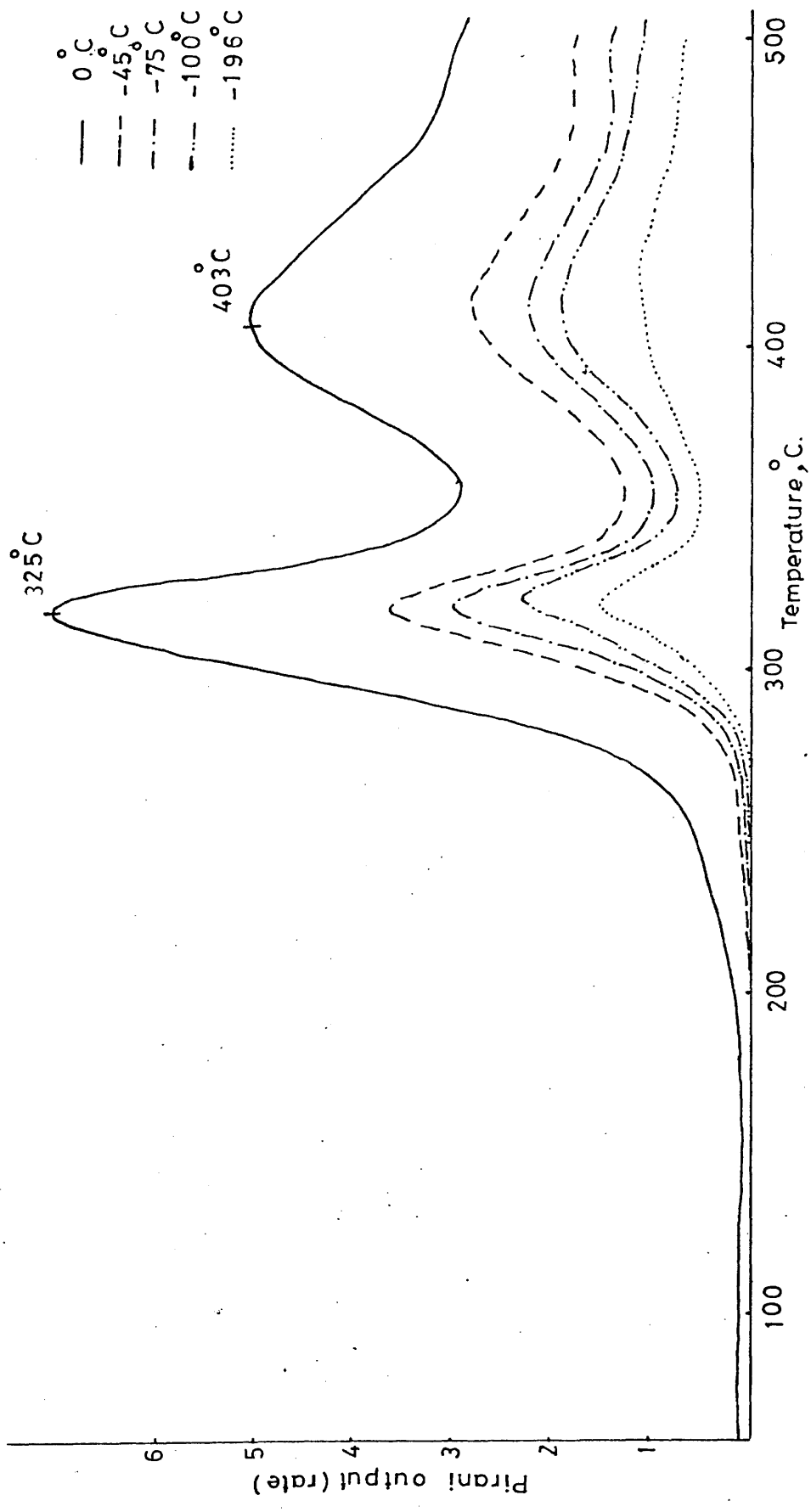


Fig.7.14. T V A thermogram for A_{27} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

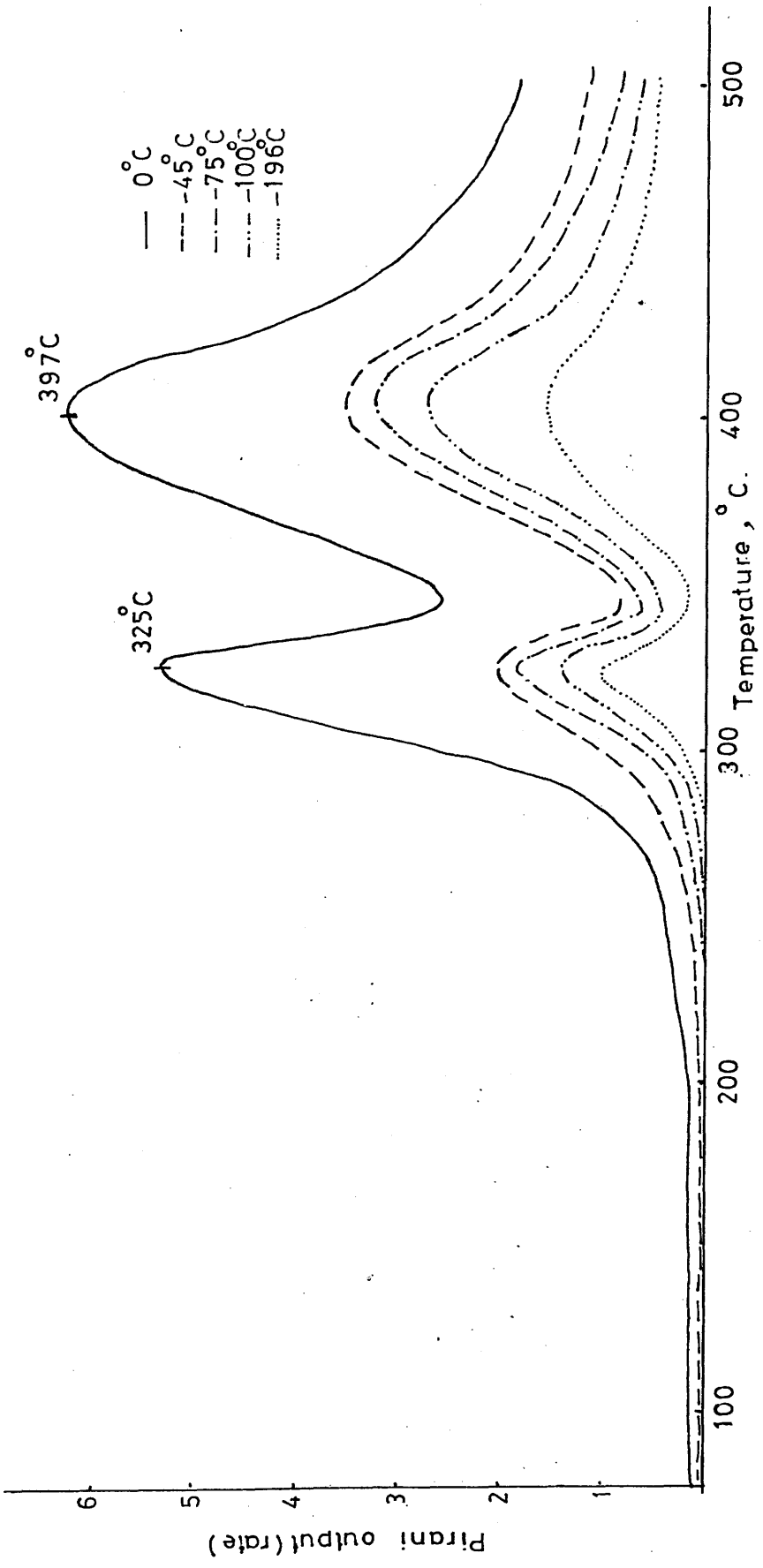


Fig.7.15. T V A thermogram for A_{28} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

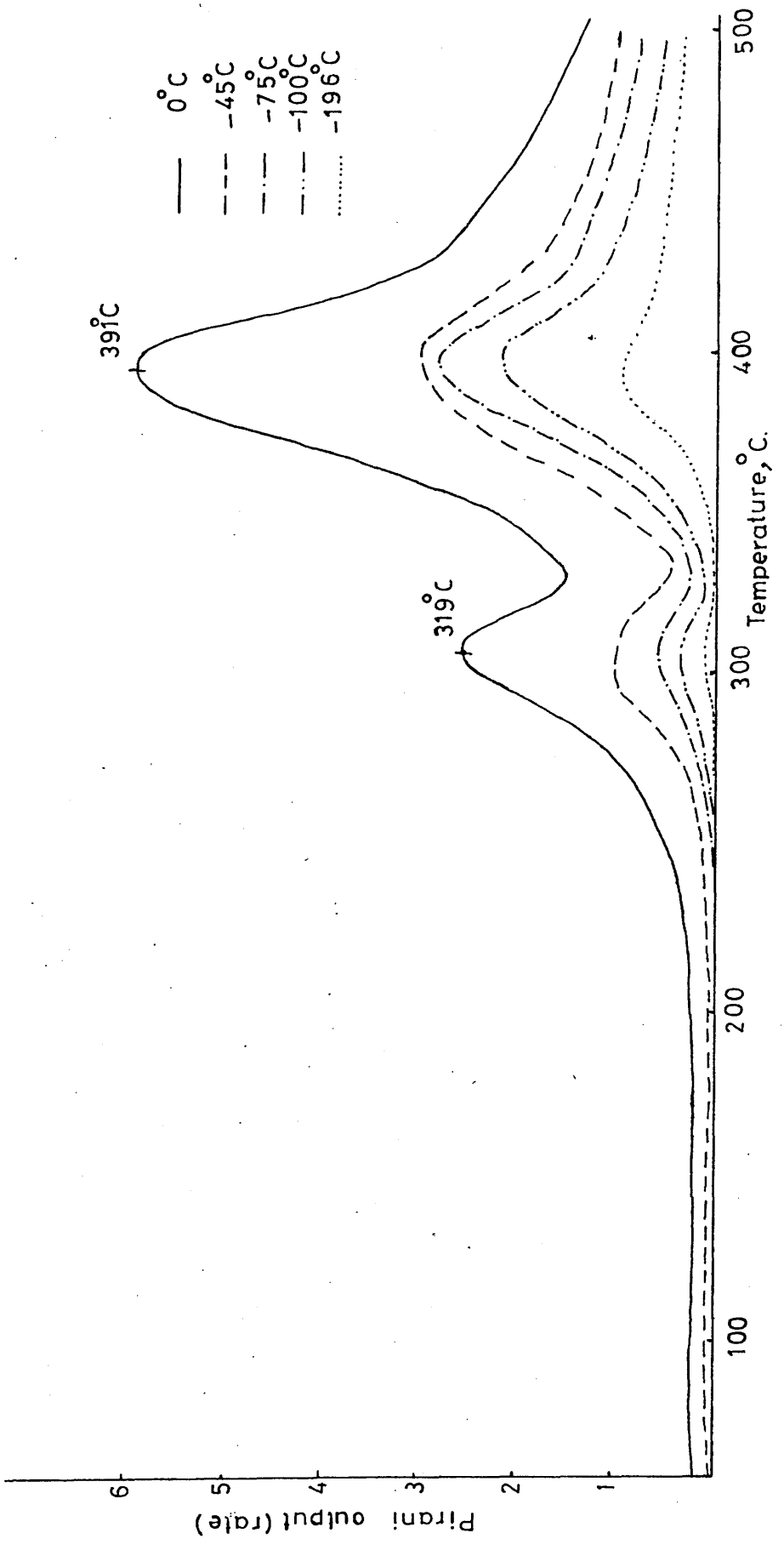


Fig.7.16. T V A thermogram for A_{29} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

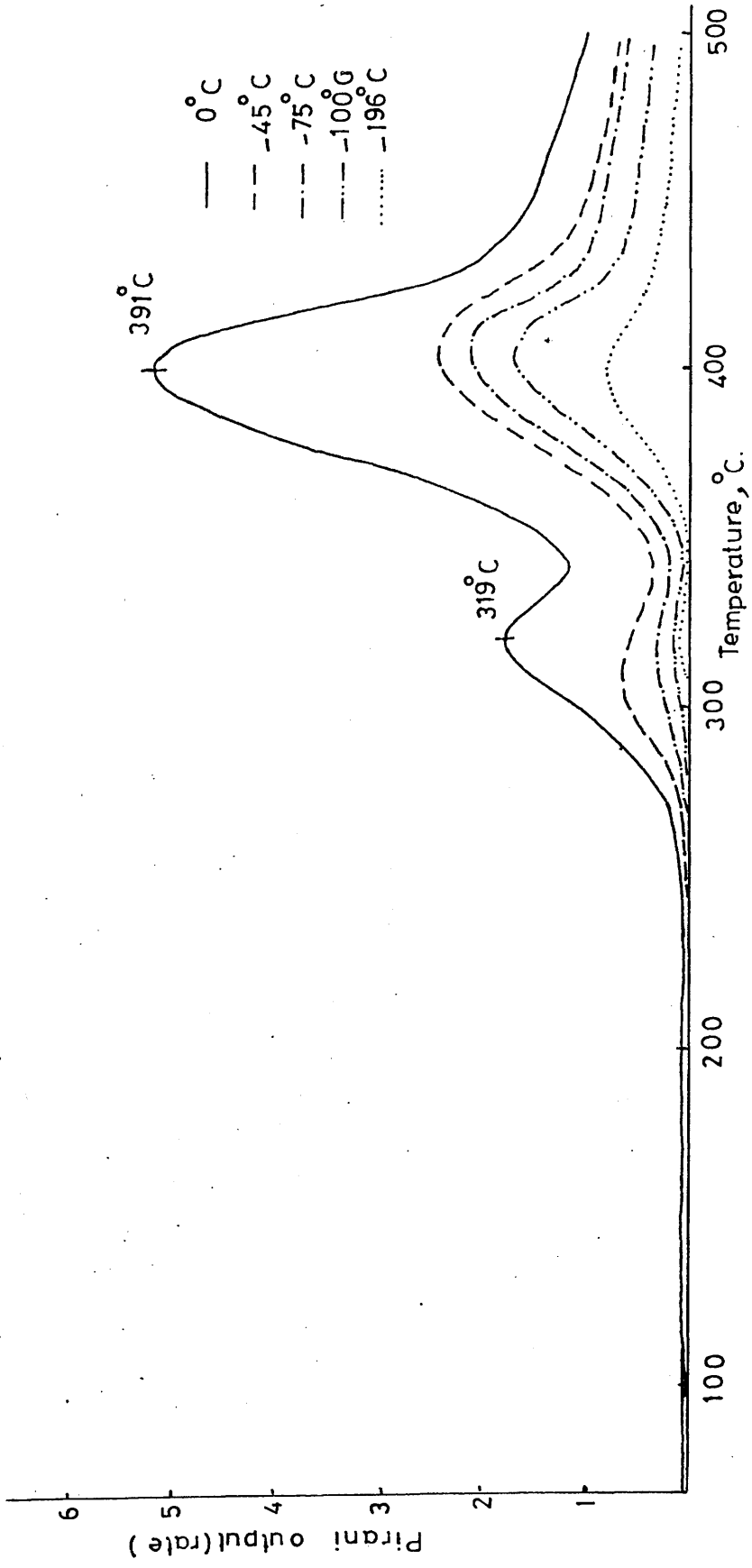


Fig.7.17. T V A thermogram for A_{30} copolymer, sample size 50 mg ; heating rate 10^{o}/min.

and 410°C. All the traces are separated to some extent, suggesting that products with a range of volatilities are being evolved. In addition, a non-condensable fraction, a cold ring fraction and a small amount of residue are formed.

iii. T G and D S C

T G curves for the 2,3 - D B P A - M A copolymers are illustrated in figure 7.18. There are two stages of weight loss, the relative importance of each stage being dependant on the copolymer composition. Table 7.6 shows the percentage weight loss of each copolymer in each stage. The stabilities of these copolymers are intermediate between the stabilities of the 2,3 - D B P A and M A homopolymers.

Table 7. 6. Percentage Weight Loss and T_{max} for each stage of degradation of 2,3 - D B P A - M A Copolymers

Polymer	First stage		Second stage		% of weight remaining at 500°C
	T_{max}, °C	Weight loss (%)	T_{max}, °C	Weight loss (%)	
A_{26}	340	72	430	15	13
A_{27}	340	63	425	24	13
A_{28}	335	45	416	46	9
A_{29}	335	22	416	68	10
A_{30}	346	20	416	74	6

D S C curves (figure 7.19) show two endothermic peaks, between 320° - 335°C for the first stage and between 410° - 420°C for the second stage. The relative importance of the stages is dependant on the

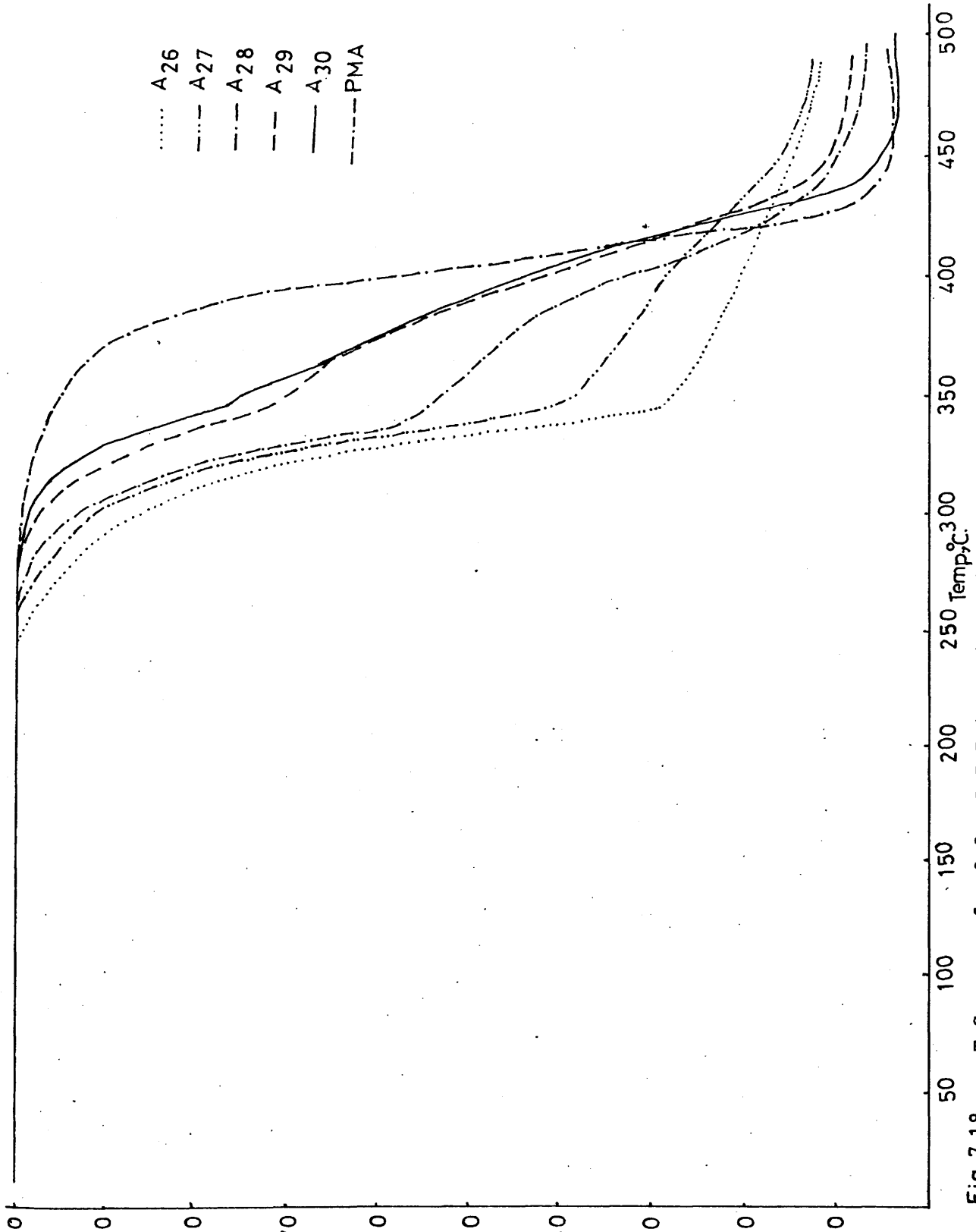


Fig.7.18. T G curves for 2,3 - D B P A - M A copolymers.

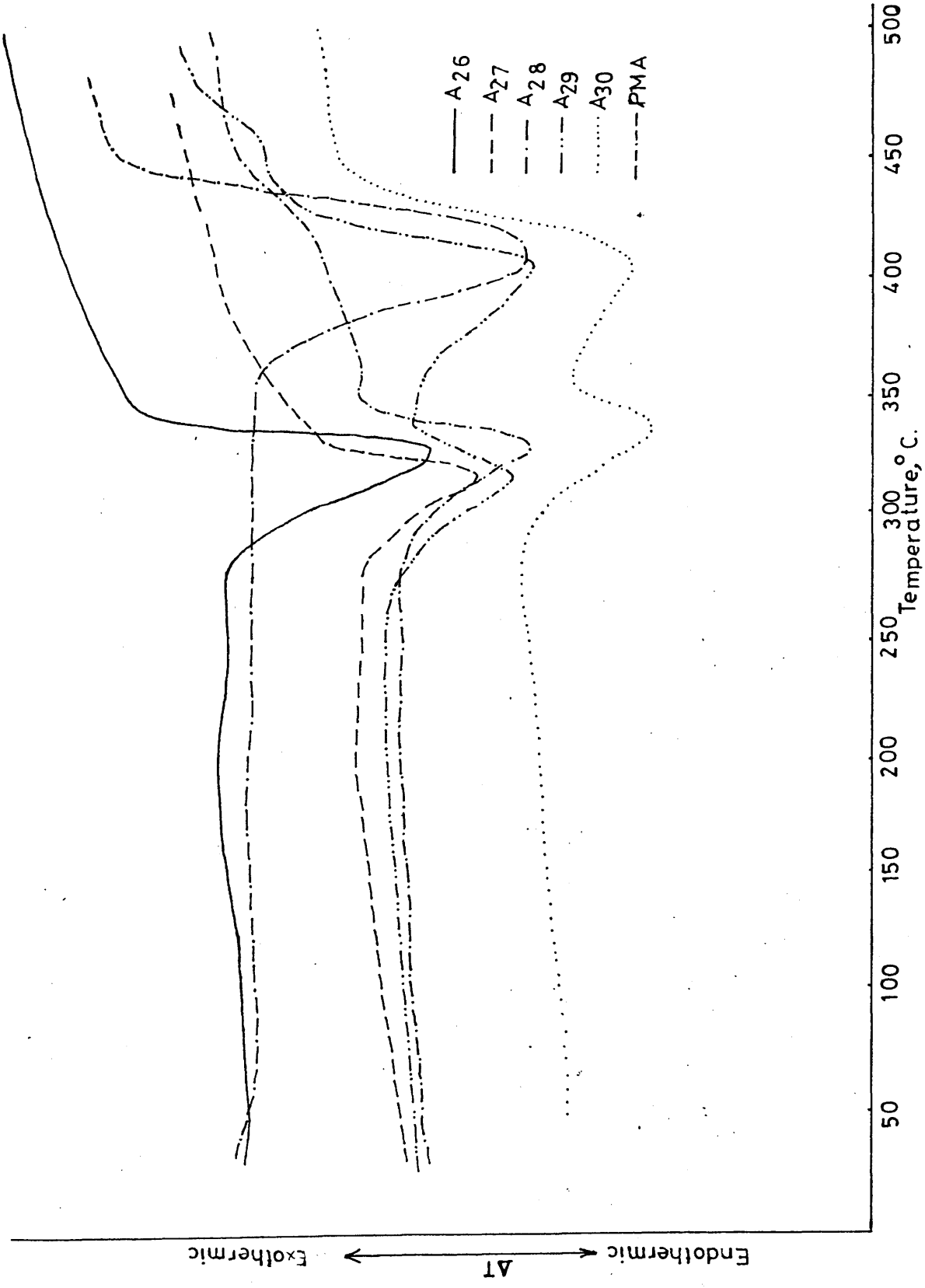


Fig. 7.19. D S C curves for 2,3 - D B P A - M A copolymers.

copolymer composition. The glass transition temperature in each case is lower than ambient temperature.

iv. Subambient T V A and Product Analysis

a. The i r and mass spectra reveal carbon dioxide, methane, propene and hydrogen in the non-condensable fraction.

b. Infra-red spectroscopy indicates that the cold ring fraction contains polymethacrylic anhydride structures and chain fragments.

c. The residue on the base of the degradation tube has no well defined i r spectral features and is assumed to be principally carbon.

d. Condensable materials were separated by subambient T V A. Figure 7.20 shows the seven peaks formed as a result of S A T V A experiments carried out on 2,3 - D B P A - M A copolymers. I r spectroscopy and mass spectrometry were used to identify the products in peaks 1, 2 and 3, while g l c and mass spectrometry were used for peaks 4, 5, 6 and 7, as shown in figure 7.21. A complete list of the products of degradation of 2,3 - D B P A - M A copolymers is shown in Table 7. 7. The products indicated by * have been inferred from mass spectral data in the absence of reference compounds for comparison.

The stepwise degradation procedure described in Chapter 4, was carried out on a single sample of A_{28} copolymer in the S A T V A apparatus. The temperatures of the stages ranged from 250°C to 500°C and the series of S A T V A curves obtained is shown in figure 7.22. The methyl bromide peak first appeared at 280°C, with two maxima at 330°C and 360°C. The methanol peak first appeared at 350°C, again indicating its association with the second stage of degradation.

v. Quantitative Measurement of the Degradation Products

Table 7. 8 lists the results of quantitative measurement of the degradation products of 2,3 - D B P A - M A copolymers. The products indicated by * should not be regarded as having been conclusively identified.

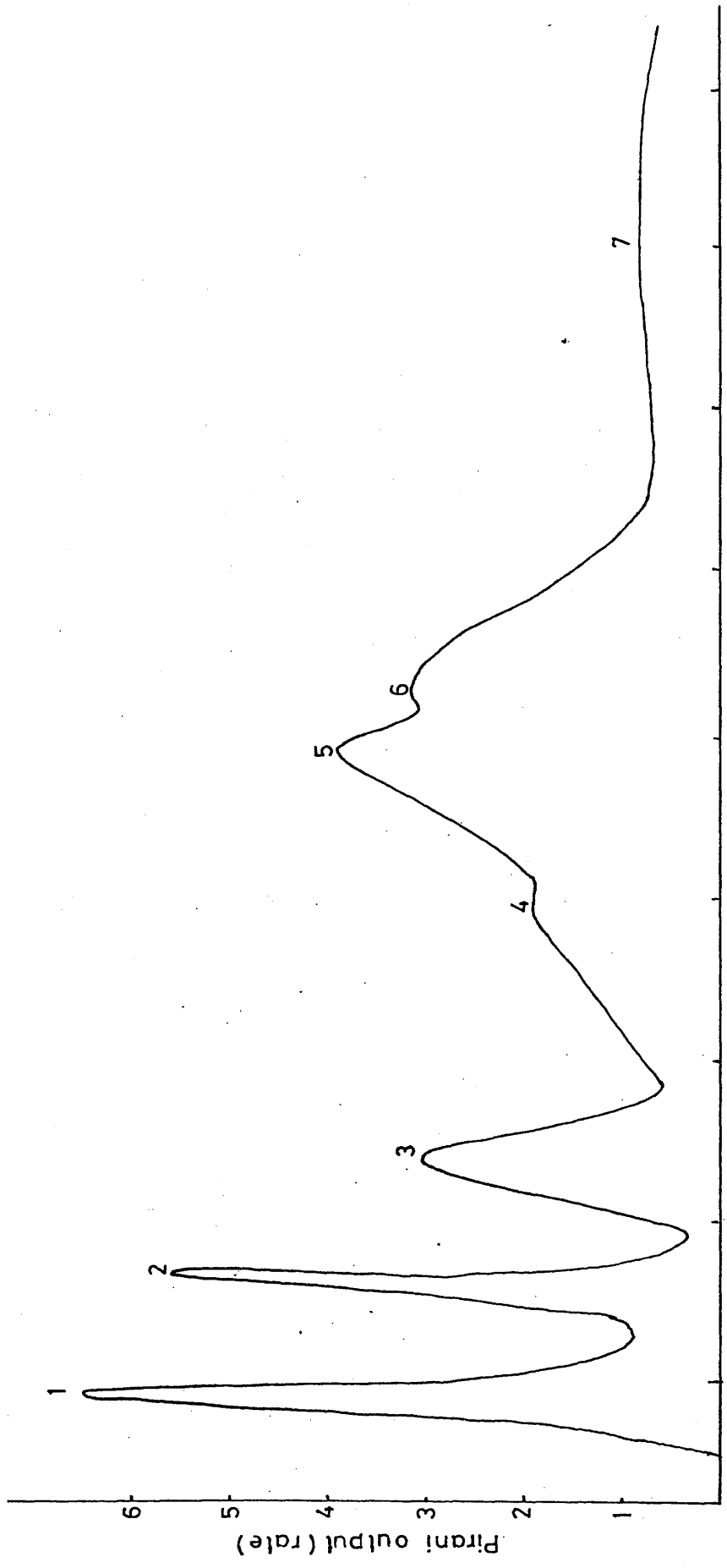
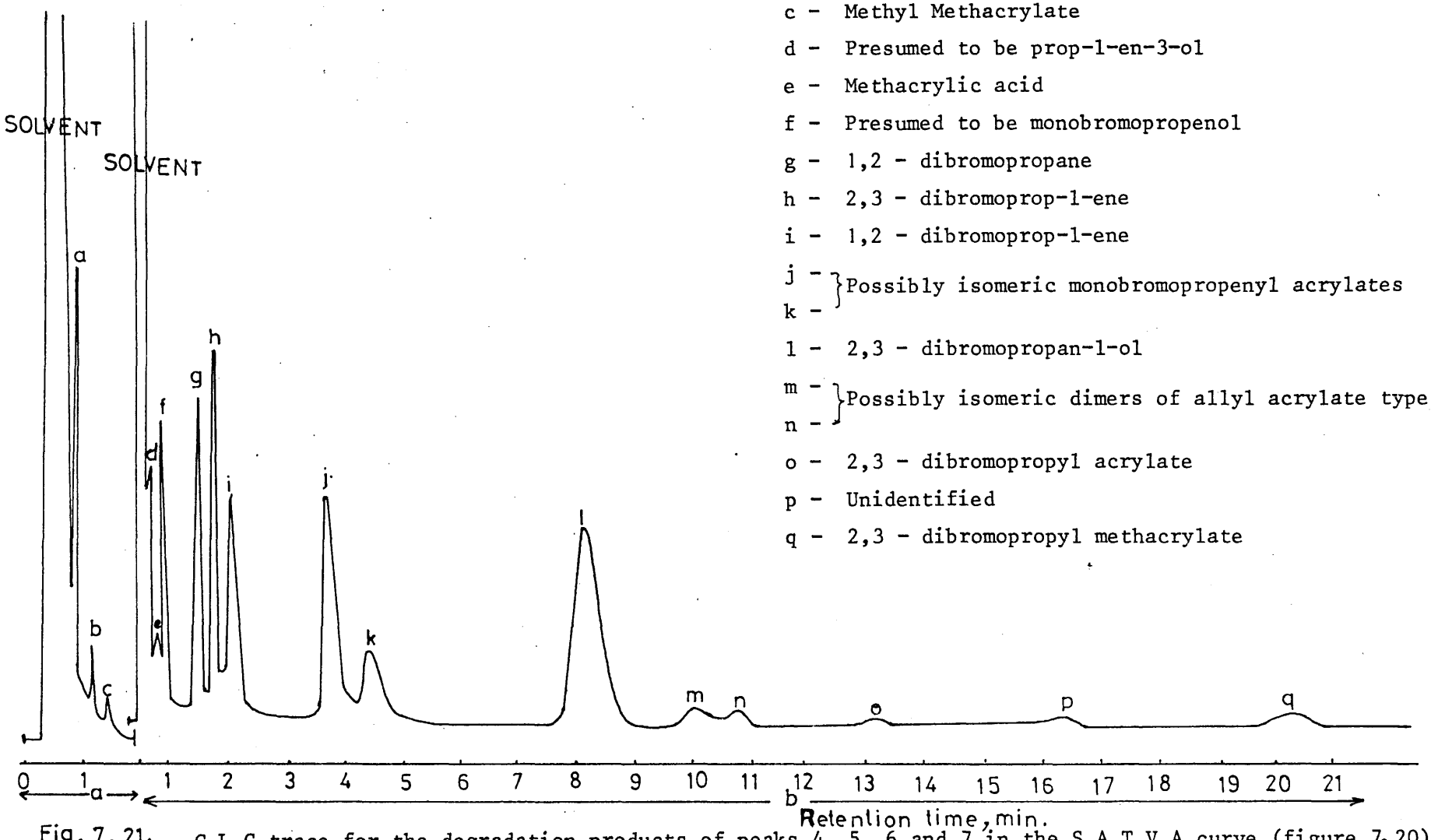


Fig.7.20. Subambient T V A curve for degradation products of 2,3 - D B P A - M A copolymers (A_{28}) from programmed degradation under vacuum to 500°C at 10°/min , 50 mg sample.



a - Methanol
b - Methyl acrylate
c - Methyl Methacrylate
d - Presumed to be prop-1-en-3-ol
e - Methacrylic acid
f - Presumed to be monobromopropenol
g - 1,2 - dibromopropane
h - 2,3 - dibromoprop-1-ene
i - 1,2 - dibromoprop-1-ene
j - } Possibly isomeric monobromopropenyl acrylates
k - }
1 - 2,3 - dibromopropan-1-ol
m - } Possibly isomeric dimers of allyl acrylate type
n - }
o - 2,3 - dibromopropyl acrylate
p - Unidentified
q - 2,3 - dibromopropyl methacrylate

Fig. 7.21. G L C trace for the degradation products of peaks 4, 5, 6 and 7 in the S A T V A curve (figure 7.20) using 5 ft. ¼ inch diameter, 10% microwax on cromosorb column isothermally at a) 90°C b) 140°C.

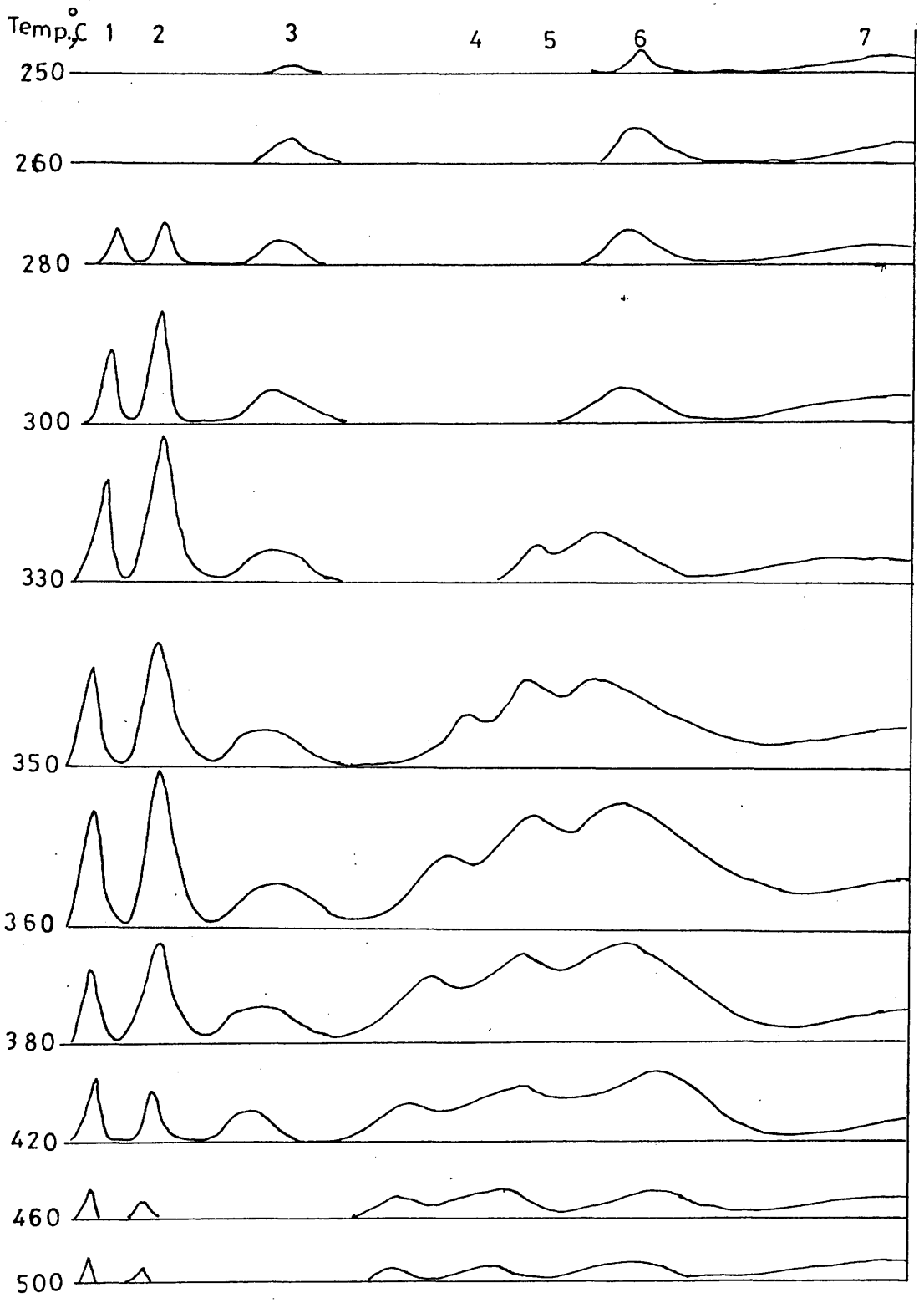


Fig.7.22. S A T V A curves fordegradation of a single sample of A_{28} copolymer (from ambient to successively higher temperature at 10^{o}/min , 50 mg sample size). Sample held at each temperature while products were collected for S A T V A.

Table 7. 7. Degradation products of 2,3 - D B P A - M A copolymers

Degradation fraction	Products	Methods of Analysis
Non-condensable materials	CH_4 , CO , propene, H_2	I R & M S
Cold ring fraction	Polymethacrylic anhydride, chain fragments	I R in solution
Residue	Carbon	I R (K Br disc)
Condensable materials		
Peak 1 (S A T V A)	CO_2 , HBr	I R & M S
Peak 2 (S A T V A)	CH_3 Br	I R & M S
Peak 3 (S A T V A)	Allyl bromide	I R & M S
Peak 4 (S A T V A)	Methanol	g l c & M S
Peak 5 (S A T V A)	Methyl acrylate (monomer), methyl methacrylate, H_2O	g l c & M S
Peak 6 (S A T V A)	Prop-1-en-3-ol*, methacrylic acid, monobromopropenol*, 1,2 - dibromopropane, 2,3 -dibromoprop-1-ene, 1,2 - dibromoprop-1-ene, Isomeric monobromopropenyl acrylates*	
Peak 7 (S A T V A)	2,3 - dibromopropan -1-ol, Isomeric dimeric species based on allyl acrylate *, 2,3 - dibromopropyl acrylate (monomer), 2,3 - dibromopropyl methacrylate.	g l c & M S

Table 7. 8. Quantitative analysis of the degradation products of 2,3 - D B P A - M A copolymers(20^{o} - 500^{o}C at 10^{o}C/min).

Products	A_{26}	A_{27}	A_{28}	A_{29}	A_{30}
	Wt.(%)				
HBr	2.21	1.07	trace	-	-
CO_2	7.20	7.11	7.31	7.25	7.4
Propene	0.2	0.2	0.1	0.1	0.1
CH_3 Br	25.3	19.6	13.9	6.9	3.9
Allyl bromide	4.2	3.6	2.6	1.2	0.8
CH_3 OH	2.0	2.3	2.7	6.72	9.31
Methyl acrylate (monomer)	1.9	1.7	1.4	1.1	0.9
Methyl methacrylate	-	trace	trace	trace	0.1
H_2O	trace	trace	trace	trace	trace
Prop-1-en-3-ol *	0.3	0.2	0.1	trace	-
Methacrylic acid	trace	trace	trace	trace	trace
Monobromoprop-1-en-3-ol *	0.3	0.2	trace	trace	-
1,2-dibromopropane	1.5	1.3	1.0	0.5	0.4
2,3-dibromoprop-1-ene	1.9	1.6	1.2	0.9	0.6
1,2-dibromoprop-1-ene	1.8	1.4	0.9	0.7	0.5
Isomeric monobromopropenyl acrylates *	1.9	1.6	1.1	0.8	0.5
2,3-dibromopropan-1-ol	1.2	0.8	0.2	0.1	-
Isomeric dimers of allyl acrylate *	0.6	0.4	0.3	0.2	0.1

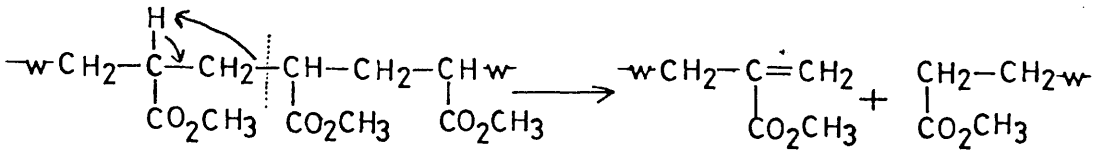
Continuation of

Table 7. 8. Quantitative analysis of the degradation products of 2,3 - D B P A - M A copolymers (20^{o} - 500^{o} C at 10^{o}/min).

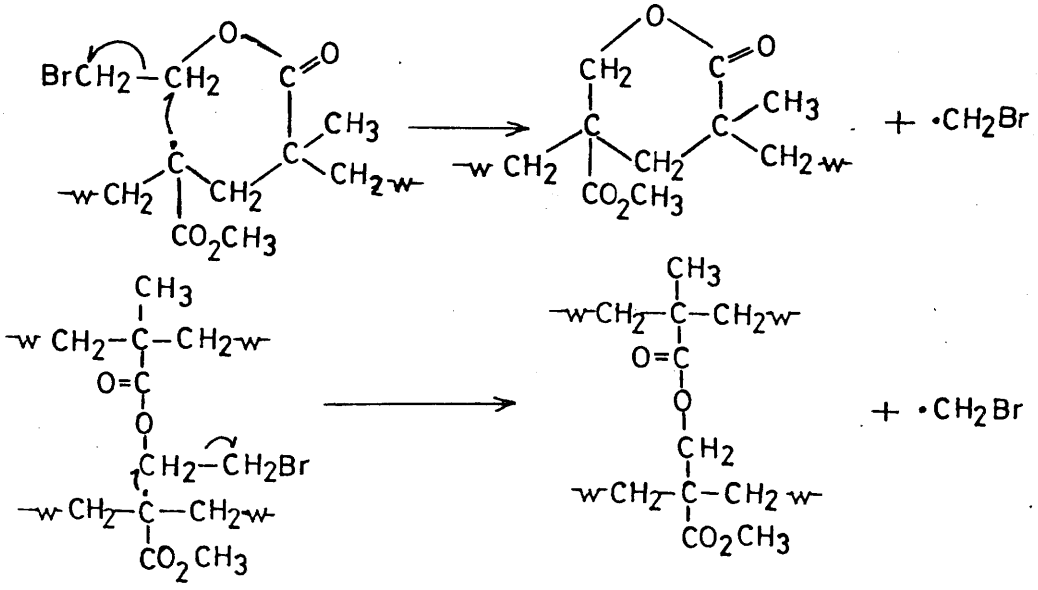
Products	A_{26}	A_{27}	A_{28}	A_{29}	A_{30}
	Wt.(%)				
2,3-dibromopropyl acrylate (monomer)	0.9	1.2	1.5	1.7	1.7
2,3-dibromopropyl methacrylate	trace	trace	trace	trace	trace
C R F	42.1	49.3	57.3	63.9	67.7
Residue	2	2	2	2	2
Total product	97.51	95.58	93.61	94.07	96.01

7. 4 DISCUSSION

In discussing the mechanisms of thermal degradation of P M A, Modorsky[59] concluded that because little monomer is formed the mechanism reactions do not involve free radicals, but may be explained by the following disproportionation reaction



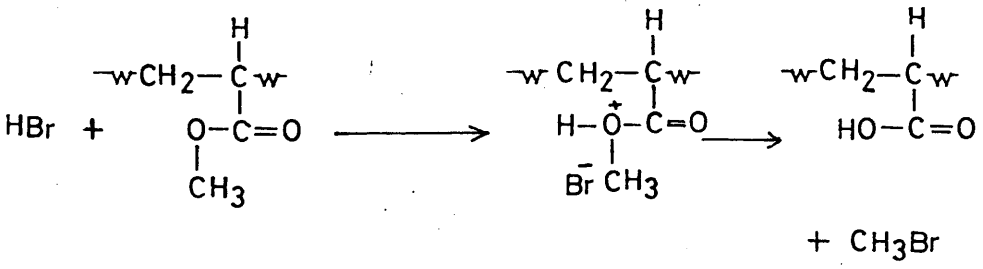
Cameron and Kane[28] concluded that their results supported Modorsky's view of a random chain scission process, but did not exclude the possibility of weak links. The same authors suggested that the low-polymer fraction may be explained by random homolytic back-bone scission followed by a free radical chain of transfer reactions. In the thermal degradation of 2-bromoethyl methacrylate - methyl acrylate copolymers Grassie and co-workers[25] found methyl bromide and 1,2-dibromoethane among the degradation products, and they suggested that both intramolecular and intermolecular reactions may occur to produce bromomethyl radicals. The following reactions were suggested :



In discussing the detailed reaction mechanisms, it is convenient to consider the two copolymer systems separately.

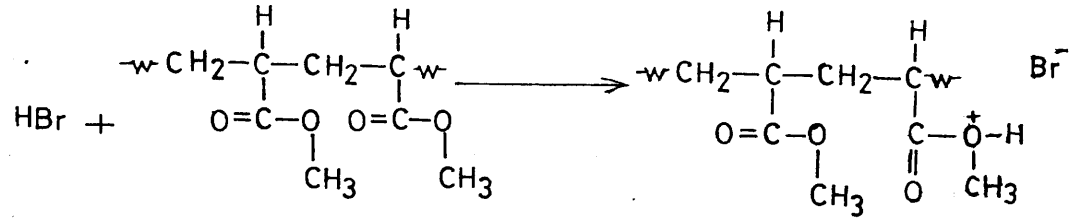
i. 2,3 - D B P M - M A Copolymers

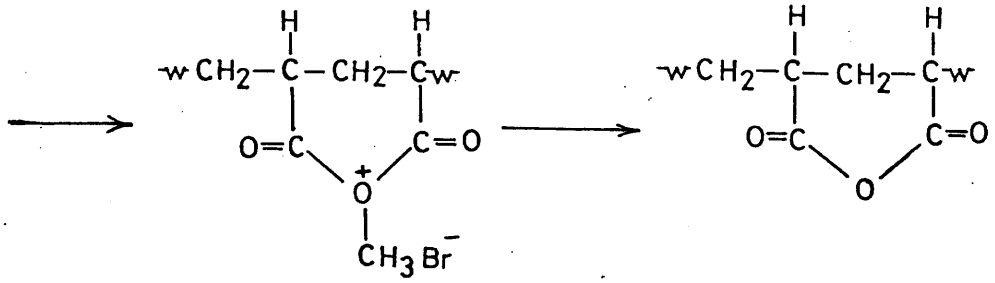
The dominant degradation products are 2,3 - D B P M monomer, and chain fragments. As the proportion of 2,3 - D B P M units in the copolymer increases, the amount of 2,3 - D B P M monomer in the degradation products increases, and the quantity of chain fragments decreases. This observation reflects the general characteristic mode of polymethacrylate and polyacrylate degradation behaviours. Methyl bromide formation during the degradation of 2,3 - D B P M - M A copolymers reaches a maximum in copolymer A_{23} . The mechanism suggested for the formation of CH_3Br is the same as already proposed for the 2,3 - D B P M - M M A copolymer system and is based on HBr attack at the methyl group in the methyl acrylate units in the chain to form CH_3Br



CH_3Br formation reaches a maximum when the proportion of 2,3 - D B P M - M A bonds in the copolymer reaches a maximum showing comparable behaviour to that already reported for the 2,3 - D B P M - M M A system. Table 7. 9 presents data on the sequence distribution of monomer units in the copolymers using Harwood's equation[38], which requires

reactivity ratio values, monomer mixture compositions and copolymer composition date. These data show that the A_{23} copolymer has more 2,3 - D B P M - M A bonds than the other copolymers and, as has already been observed, this copolymer gives more CH_3Br than the other copolymers.Methanol is formed during the degradation of P M A as a result of the formation of an alkoxy radical[29]. Grassie[24] found that three adjacent methyl acrylate units are required for the formation of methanol. In the same way, in the degradation of 2,3 - D B P M - M A copolymers, methanol can be formed as a result of alkoxy radical formation. As an alternative, methanol can also be formed by attack of HBr on the methyl group in methyl acrylate as described earlier for the 2,3 - D B P M - M M A copolymer system.





$+ CH_3OH$ $+ CH_3Br$

Table 7. 9. Data on sequence distribution in copolymers A_{21} , A_{22} , A_{23} , A_{24} and A_{25}

Copolymer Composition A-B %	A-A bond in copolymer %	A-B and B-A bond in copolymer %	B-B bond in copolymer %	A-A-A triads (f_{AAA})	B-A-A and A-A-B triads (f_{BAA})	B-A-B triads (f_{BAB})
A_{21} 83-17	67.5	31.01	1.5	0.661	0.304	0.035
A_{22} 70-30	48.54	42.32	8.54	0.481	0.425	0.094
A_{23} 51-49	23.98	54.04	21.98	0.221	0.498	0.281
A_{24} 28-72	5.86	44.28	49.86	0.044	0.331	0.625
A_{25} 18-82	2.71	30.58	66.71	0.023	0.256	0.722

A : 2,3 - D B P M & B : M A

The symbol f denotes the fraction of A monomer to be found in the middle of the triads AAA, BAA and (AAB) and BAB.

As indicated in figure 7.11 the methyl bromide peak shows two maxima, suggesting that there are two distinct mechanisms responsible for its formation. It would be expected that the concentration of polymethacrylic anhydride structures would also reach a maximum in copolymer A_{23}, but this is difficult to confirm, since the cold ring fraction contains chain fragments other than those of the anhydride type. The stability of the copolymers is intermediate between P2,3 - D B P M and P M A homopolymers as shown in figure 7.6. It is clear that, even when stabilising anhydride linkages have formed in the degrading copolymers, their effect is still not great enough to give stability comparable to that of P M A itself. All other products formed in the degradation of P2,3 - D B P M and P M A homopolymers are formed also in the degradation of 2,3 - D B P M - M A copolymers, the different percentages depending on the copolymer composition. The yield of methyl acrylate monomer increases with decreasing concentrations of acrylate in the copolymer. This effect was also observed by Grassie[24] in the degradation of M M A - M A copolymers.

ii. 2,3 - D B P A - M A Copolymers

The dominant degradation products are methyl bromide and a cold ring fraction which contains polymethacrylic anhydride structures and chain fragments. All other products formed in the degradation of P2,3 - D B P A and P M A homopolymers are formed also in the degradation of 2,3 - D B P A - M A copolymers, the different percentages depending on the copolymer composition. Methyl bromide formed during the degradation of 2,3 - D B P A - M A copolymers is thought to be formed by the mechanisms discussed earlier, based on HBr

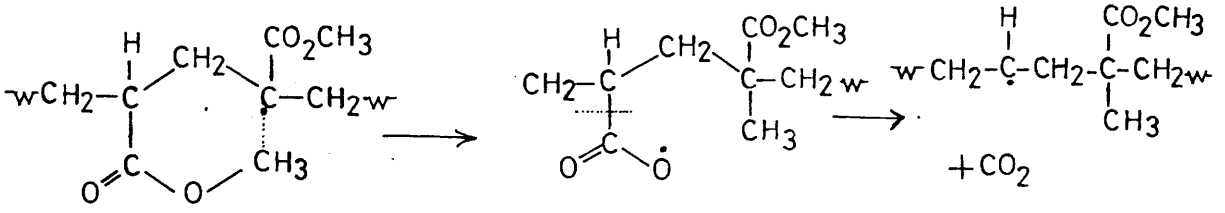
Table 7 . 10. Data on sequence distribution in copolymers A_{26} , A_{27} , A_{28} , A_{29} and A_{30}

Copolymer Composition A-B %	A-A bond in copolymer %	A-B and B-A bond in copolymer %	B-B bond in copolymer %	A-A-A triads (f_{AAA})	B-A-A and A-A-B triads (f_{BAA})	B-A-B triads (f_{BAB})
A_{26} 52-48	17.625	68.75	13.625	0.115	0.448	0.437
A_{27} 42-58	8.635	66.73	24.635	0.042	0.327	0.631
A_{28} 30-70	3.56	52.88	43.56	0.014	0.209	0.777
A_{29} 14-86	0.875	26.25	72.875	0.004	0.117	0.879
A_{30} 9-91	0.225	17.55	82.225	0.001	0.049	0.95

A : 2,3 - D B P A & B : M A

The symbol f denotes the fraction of A monomer to be found in the middle of the triads AAA, BAA and (AAb) and BAB.

attacking the methyl group of a M A unit to form CH_3Br. Copolymer A_{26} produces 25.3% of CH_3Br on degradation; this is more than any of the other copolymers, and again A_{26} is seen to have more 2,3 - D B P A - M A bonds than the other copolymers. Table 7. 10 contains the sequence distribution data for all the copolymers. Methanol formation can be explained using the same mechanism as for the 2,3 - D B P M - M A copolymer system. Carbon dioxide production shows a fairly constant yield at different copolymer compositions, and this is not surprising in view of the fact that the CO_2 yields from P2,3 - D B P A and P M A homopolymers are nearly the same. The mechanism suggested for CO_2 formation during the degradation of P M A[29,60] is represented as follows:-



The mechanism, together with that suggested earlier for CO_2 formation during the degradation of P2,3 - D B P A, are sufficient to explain CO_2 formation. The production of either monomer is greatest when its concentrationin the copolymer is smallest. The stability of these copolymers are intermediate between P2,3 - D B P A and P M A homopolymers as shown in figure 7.18. Again the stability imparted to the degrading copolymers by anhydride structures is insufficient to give stability comparable to that of P M A itself.

CHAPTER 8

THERMAL DEGRADATION of BLENDS of P2,3 - D B P M and P2,3 - D B P A with P M M A and P M A

8. 1 INTRODUCTION

In Chapters 5 and 7, it has been shown that the thermal degradation behaviour of 2,3 - D B P M and 2,3 - D B P A units can be greatly influenced by the presence of M M A and M A groups in the copolymer chain. In this chapter a study will be described of some polymer blends in order to compare the degradation behaviours of these blends with those of the copolymers, and to determine whether there is any evidence of interaction between the polymers in the blends. P2,3 - D B P M - P M M A, P2,3 - D B P M - P M A, P2,3 - D B P A - P M M A and P2,3 - D B P A - P M A blends were studied by the T V A and S A T V A techniques, their degradation products reported either qualitatively or quantitatively. The blends were studied in the form of thin films cast on to the bottom of the degradation tube by the method outlined in Chapter 2. Only 1 : 1 blends (by weight) were investigated, each film being pre-heated to 120°C for one hour to remove residual solvent. In this way transparent films were obtained indicating reasonable compatibility with good dispersion of the two polymer phases.

8. 2 THERMAL METHODS OF ANALYSIS

i. Thermal Volatilisation Analysis (T V A)

Film samples (25 mg of each polymer) were heated from ambient temperature to 500°C at 10°C/min. T V A traces of P2,3 - D B P M - P M M A, P2,3 - D B P M - P M A, P2,3 - D B P A - P M M A and P2,3 - D B P A - P M A blends are shown in figures 8.1, 8.2, 8.3 and 8.4 respectively.

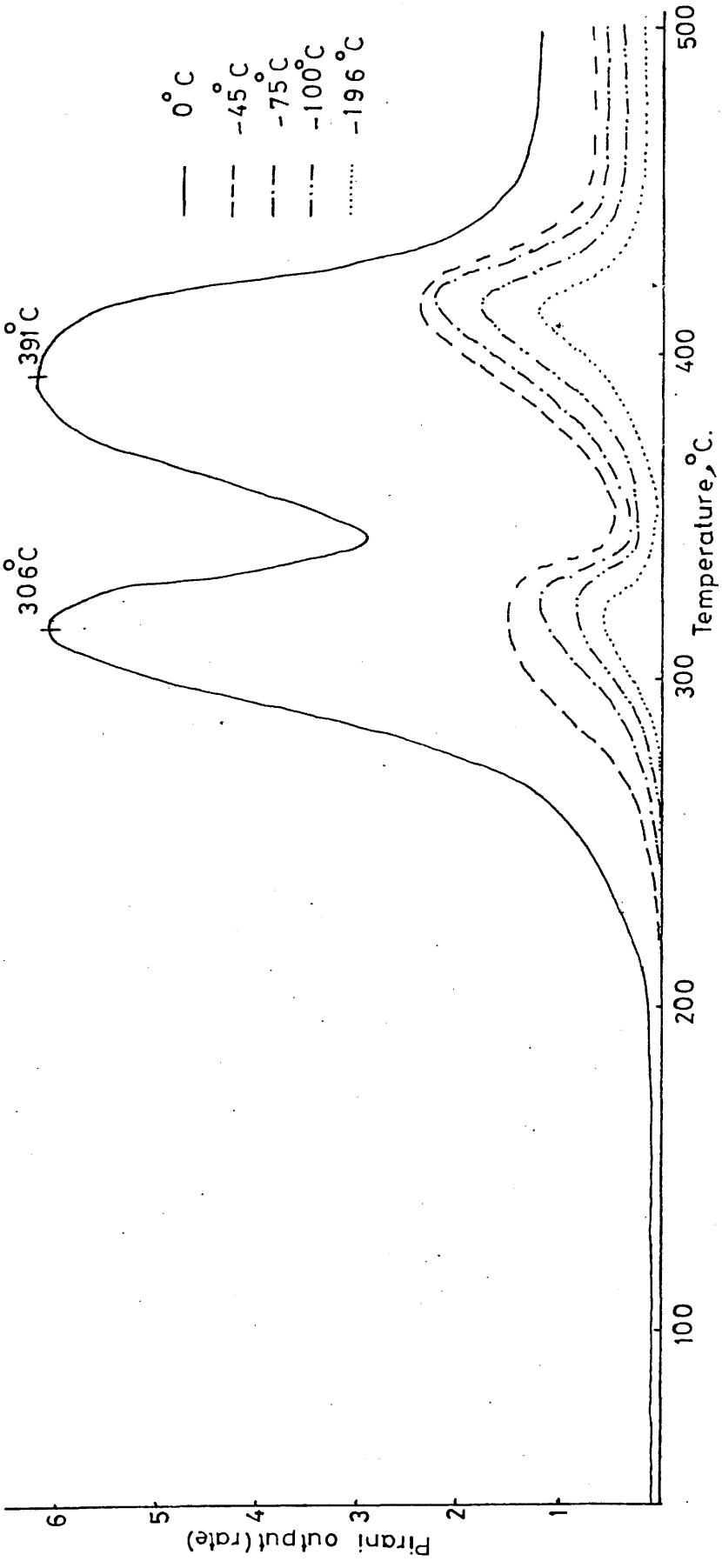


Fig. 8.1. T V A thermogram for P2,3 - D B P M - P M M A blend (1:1), sample size 25 mg of each polymer; heating rate 10^{o}/min.

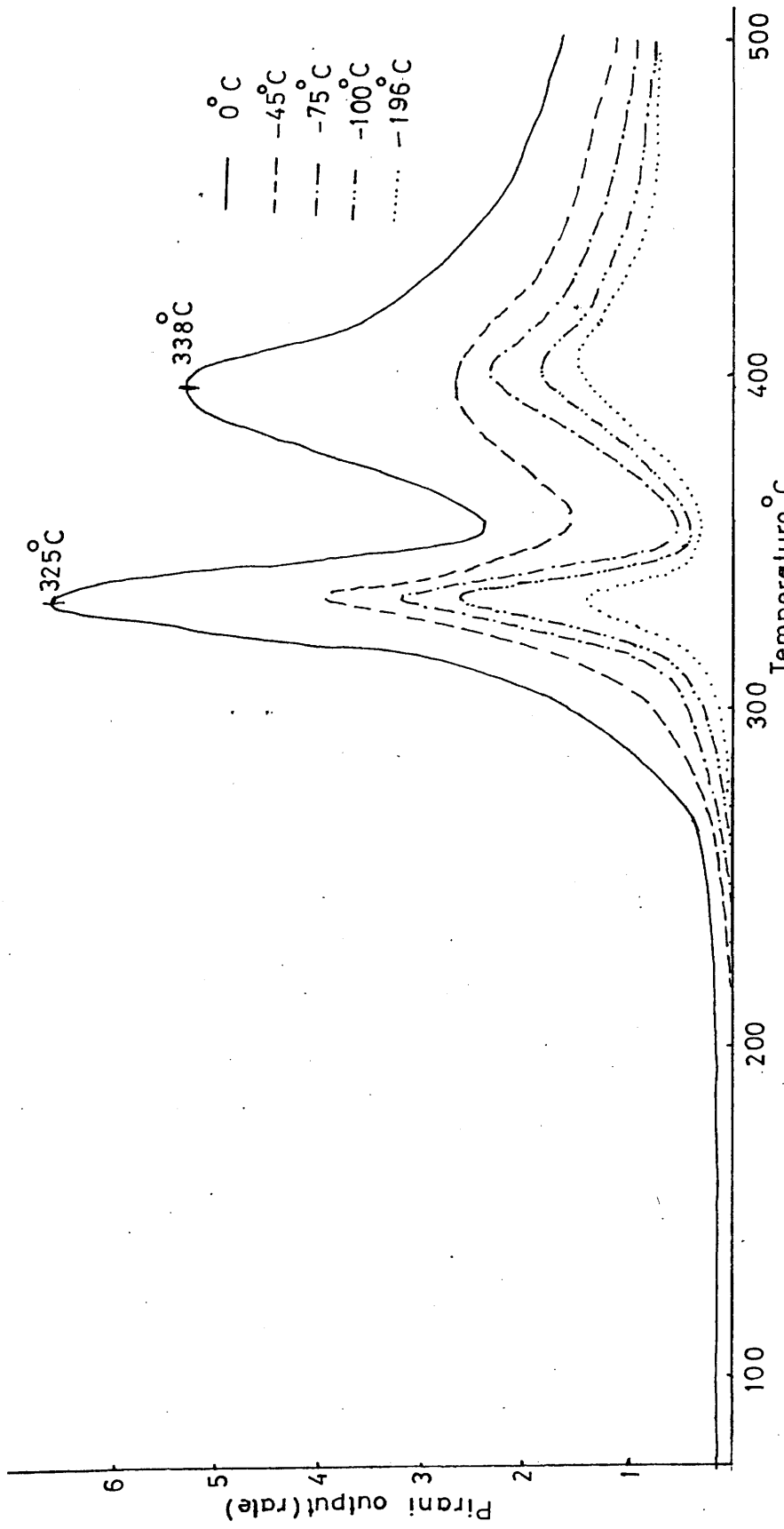


Fig.8.2. T V A thermogram for P2,3 - D B P M - P M A blend (1:1), sample size 25 mg of each polymer; heating rate 10^{o}/min.

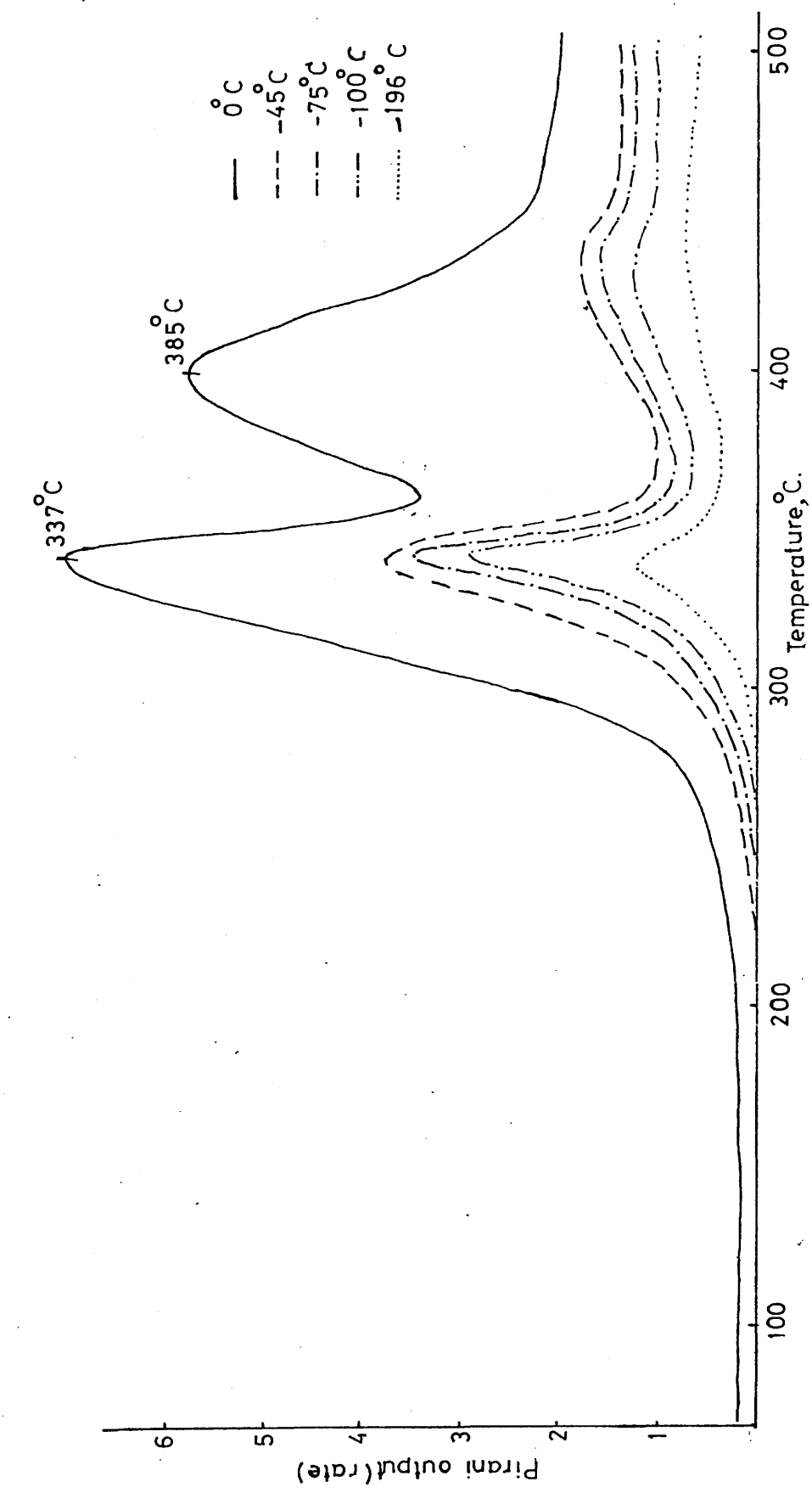


Fig. 8.3. T V A thermogram for P2,3 - D B P A - P M M A blend (1:1), sample size 25 mg of each polymer; heating rate 10°/min.

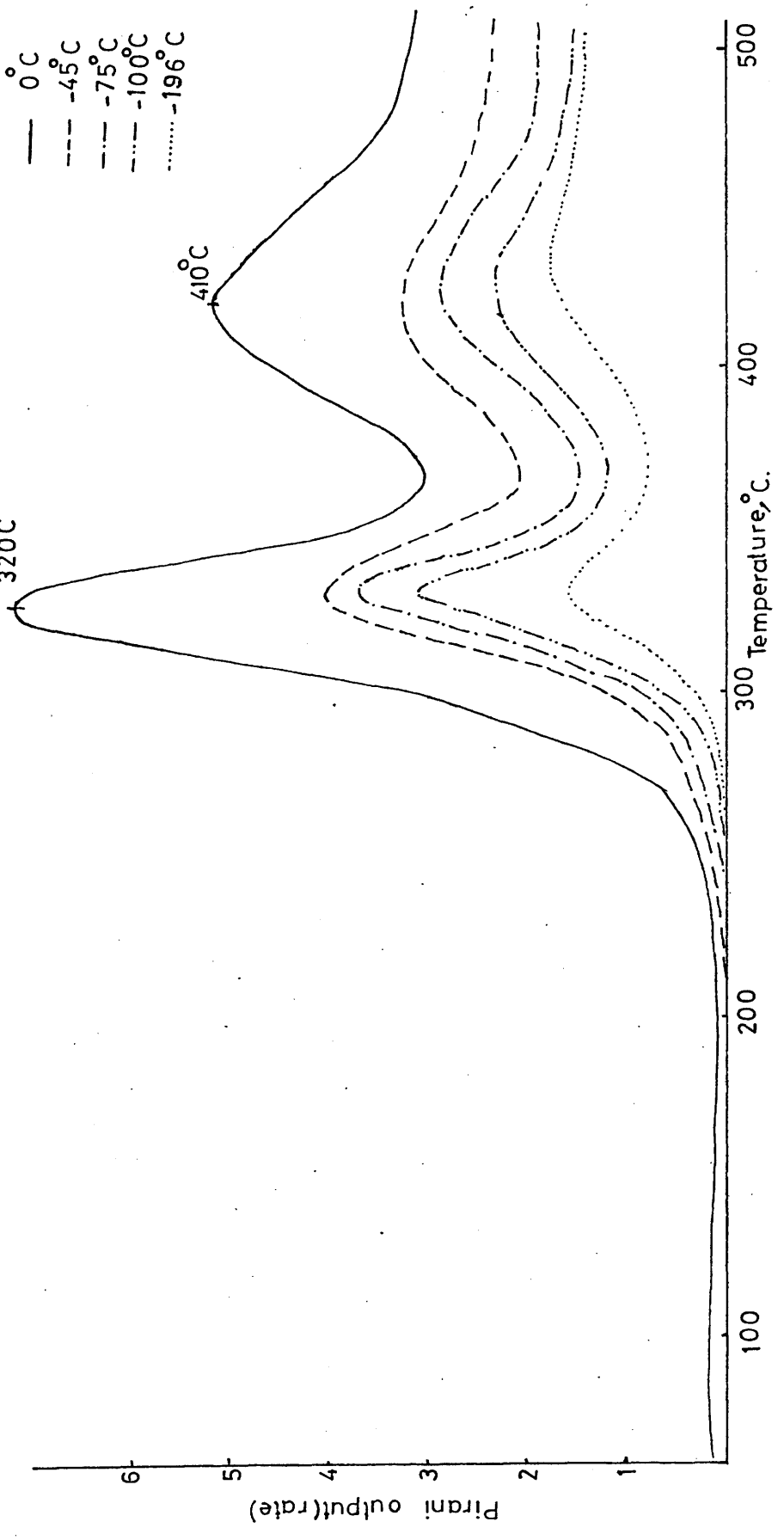


Fig.8.4. T V A thermogram for P2,3 - D B P A - P M A blend (1:1), sample size 25 mg of each polymer; heating rate 10^{o}/min.

In each case there are two distinct peaks with a separation of traces which indicates that there are products with a wide range of volatilities. There is also a considerable amount of non-condensable material as well as a yellow cold ring fraction and a small amount of residue. The temperatures of T_{max} for each peak are shown on the traces, which are comparable to those of the corresponding copolymers.

ii. Subambient T V A and Product Analysis

Subambient T V A was carried on the volatile products from each film sample. The condensable volatile products were examined by infrared spectroscopy and mass spectra. The liquid products were examined by g l c and mass spectra. Figure 8.5 shows typical subambient T V A traces each of which exhibits seven peaks. It was observed that methyl bromide and methanol are formed in the degradation products suggesting that some interaction occurs between the two polymers. Tables 8.1 and 8.2 present the results of quantitative analysis of the degradation products from these blends. The products indicated by * should be regarded as speculative and have not been confirmed by reference to the pure compounds.

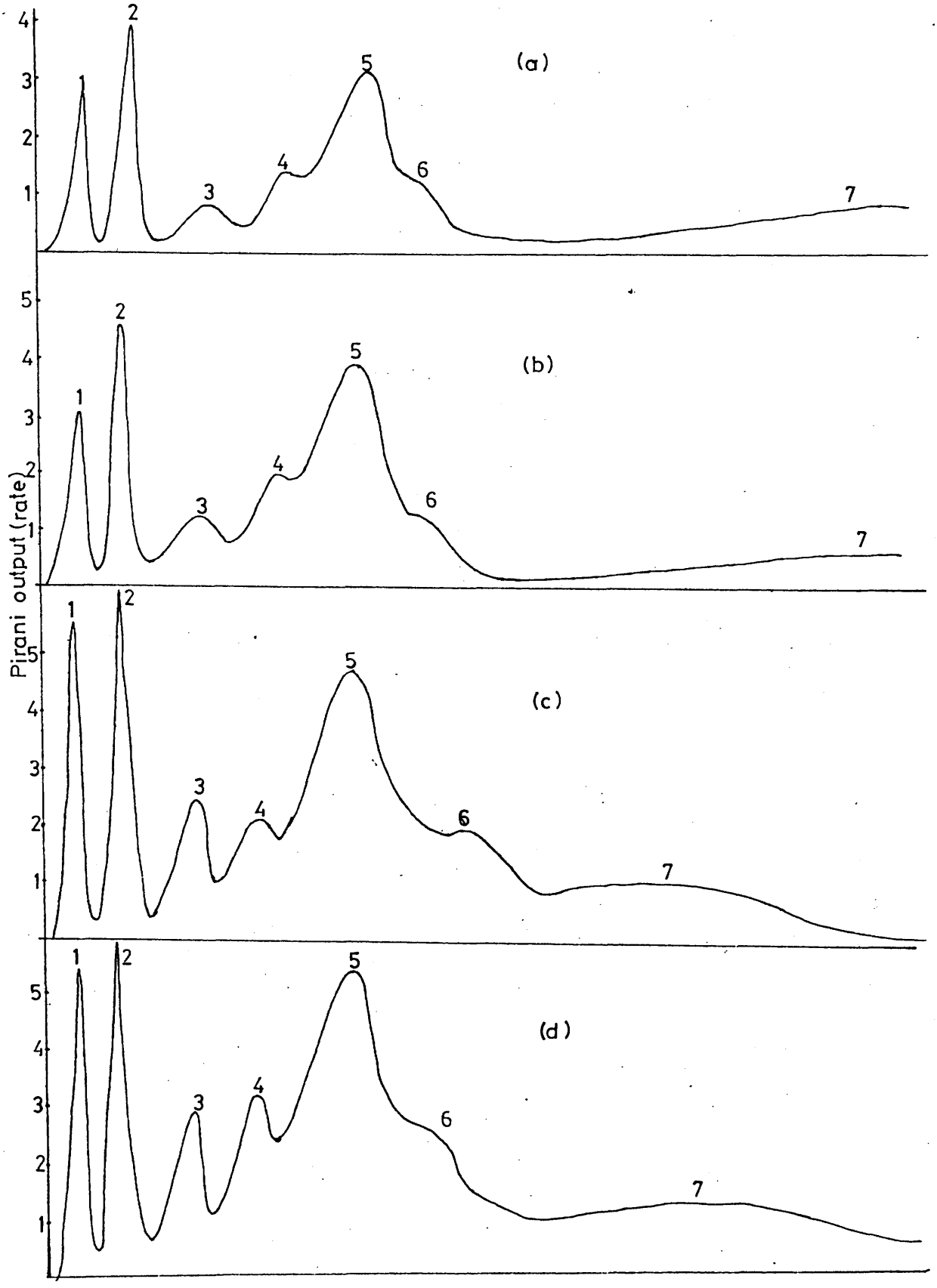


Fig. 8.5. S A T V A tracesfor the degradation products of
a. P2,3 - D B P M - P M M A b. P2,3 - D B P M - P M A
c, P2,3 - D B P A - P M M A d. P2,3 - D B P A - P M A blends.

Table 8. 1 Quantitative Analysis of the Products of Degradation of P2,3 - D B P M - P M M A and P2,3 - D B P M - P M A Blends (20^{o}-500^{o}C, at 10^{o}C/min).

Product	P2,3 - D B P M - P M M A blend	P2,3 - D B P M - P M A blend
	Wt.(%)	
HBr	2.9	3.1
CO_2	1.2	5.2
Propene	0.1	0.2
CH_3Br	3.5	3.8
Allyl bromide	1.2	1.2
CH_3OH	0.4	3.9
M M A (monomer)	43.1	trace
M A (monomer)	-	1.4
H_2O	trace	trace
Br_2	2.0	1.7
Methacrylic acid	trace	trace
Allyl methacrylate	1.5	1.7
1,2 - dibromopropane	0.2	0.2
Isomeric dibromopropenes	0.3	0.4
Isomeric monobromopropenyl methacrylates *	0.6	0.5
2,3 - D B P M (monomer)	29.3	28.1
C R F (Poly methacrylic anhydride)	8.5	38.9†
Residue	4	4
Total products identified	98.8	94.3

† C R F contains Polymethacrylic anhydride + chain fragments.

Table 8. 2 Quantitative Analysis of the Products of Degradation of P2,3 - D B P A - P M M A and P2,3 - D B P A - P M A blends (20^{o}-500^{o}C, at 10^{o}C/min).

Product	P2,3 - D B P A - P M M A blend Wt. (%)	P2,3 - D B P A - P M A blend
HBr	9.5	8.1
CO_2	4.6	7.4
Propene	0.2	0.2
CH_3Br	12.7	13.9
Allyl bromide	4.8	4.5
MeOH	0.7	4.0
M M A (monomer)	31.6	trace
M A (monomer)	-	1.3
H_2O	trace	trace
Methacrylic acid	trace	trace
Prop-1-en-3-ol *	0.4	0.4
Monobromoprop-1-en-3-ol *	0.3	0.4
1,2 - dibromopropane	1.3	0.9
2,3 - dibromoprop-1-ene	2.0	2.1
1,2 - dibromoprop-1-ene	2.1	2.2
Isomeric monobromopropenyl acrylates *	2.6	2.0
2,3 - dibromopropan-1-ol	2.5	2.0
Isomeric dimeric species based on allyl acrylates *	0.9	0.7
2,3 - D B P A (monomer)	1.2	1.1
2,3 - D B P M	trace	trace
C R F (Poly methacrylic anhydride + chain fragment)	15.9	43.6
Residue	3	4
Total product	98.3	98.8

8. 3 DISCUSSION

The formation of methyl bromide and methanol in the degradation of polyblends reveals that interaction takes place between both the brominated polymers and P M M A as well as P M A during decomposition of the blends.

In the copolymers, both monomers are part of an integrated molecular system with neighbouring units able to participate in both intra and inter molecular reactions. In the polyblend system, however, only the latter type of reaction is possible and may only occur at the phase boundaries. Thus, the compatibility and dispersion properties of the polyblend must be an important factor in the production of methyl bromide and methanol. McNeill et al[35], suggested that any interactions between polymers in a blend must take into account the physical state of the system, and under certain conditions in solution also[61,62]. He found that the compatibility of a polymer pair is dependant on a number of factors, including chemical structure, molecular weights, temperature, and (for solution) concentration. Up to the present time, no way has been found to overcome the mutual incompatibility of unlike macromolecules. It must be accepted, therefore, that any polymer blend will not form a true mixture, and certainly not a solid solution. In the solid state, small regions or micelles of one polymer will be distributed throughout the matrix of the second polymer. Any chemical interaction which takes place between the components in such a system must either take place at phase boundaries, or involve the diffusion of a species formed in one phase into the second phase. In the latter case, the smaller the diffusing species, the more easily will be able to diffuse through

the polymer network. Thus Richards and Satler[63] believe that the species initiating breakdown of polystyrene, when it is present in a blend with poly (∝- methylstyrene) are low molecular weight radicals, arising from complete unzipping of the chain in the latter polymer, rather than macroradicals. The interaction of a polymer radical with a polymer molecule of another type cannot be ruled out in all cases, however, since Mizutani[64] showed that block and graft copolymers were formed in degradation of blends of polypropylene with other polymers. The mechanisms of formation of methyl bromide and methanol from the blends may also be accounted for on the basis of attack by HBr on the methyl groups in the polymethacrylates and polyacrylates by the mechanisms described in Chapters 5 and 7. From tables 8.1 and 8.2 it is obvious that not all HBr attacks the ester groups in polymethacrylate and polyacrylate, since some remain among the degradation products. This can be explained in terms of the incompatibility of the blends.

CHAPTER 9

GENERAL CONCLUSIONS and SUGGESTION of FUTURE WORK

9. 1 GENERAL CONCLUSIONS

In the light of the experimental results described in previous chapters, a number of interesting conclusions may be drawn.

i. The reactivity ratios of dibrominated methacrylate and acrylate esters with methyl methacrylate, styrene and methyl acrylate were determined and are presented in Table 3. 3. Two different techniques were used, namely microanalysis and N M R spectroscopy, which are in good agreement.

ii. P2,3 - D B P M depolymerises to yield monomer as a major product. A small amount of ester decomposition occurs to produce HBr,CO_2, allyl bromide, bromine, anhydride and other quite complex products. The major products of degradation of P2,3 - D B P A are HBr,CO_2, allyl bromide, 2,3 - dibromopropan-1-ol, dibromopropens , chain fragment and also some quite complex products.

iii. An interaction takes place between the brominated monomer and M M A during the decomposition of the copolymers, leading to methyl bromide, methanol and anhydride structures. The yields of methyl bromide, methanol and anhydride is at a maximum when the number of adjacent 2,3 - D B P M - M M A or 2,3 - D B P A - M M A bonds is at a maximum. The mechanisms suggested for the formation of these products is based upon the attacking properties of HBr on the ester groups in methyl methacrylate.

iv. The thermal stability of these copolymers also reaches a maximum, when anhydride formation is at a maximum, suggesting that anhydride

formation has a stabilising effect on the depolymerisation reaction.

v. There is no evidence of interaction between the monomers in 2,3 - D B P M - S and 2,3 - D B P A - S copolymers, and the stabilities of these copolymers are intermediate between those of the homopolymers.

vi. Interaction also occurs during the degradation of 2,3 - D B P M - M A and 2,3 - D B P A - M A copolymers leading to methyl bromide, methanol and anhydride. Again these products are at a maximum when the proportion of adjacent 2,3 - D B P M - M A and 2,3 - D B P A - M A bonds are at a maximum.

vii. The thermal stability of these copolymers are intermediate between those of the homopolymers. It seems that P M A is more stable than the copolymer even when the copolymer contains some anhydride.

viii. Interaction also occur during the degradation of blends of the brominated polymers with P M M A and P M A resulting again in the formation of methyl bromide, methanol and anhydride.

9. 2 SUGGESTION FOR FUTURE WORK

A study of the changes in the molecular weight of the homopolymers and the copolymers at different temperature could provide useful information about the nature of decompositions which occur in these polymers.

It would also be appropriate to study the oxidation and photo-degradations of these polymers.

It will also be important to study the flammability properties of these materials in order to assess the effectiveness of bromine atoms in the polymer structure as a fire retarding agent.

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